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METAL
CONTAINING POLYMERS AS FUEL
CELL CATALYSTS

Final Report
U. S. Army Research Office

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Several aspects of the fuel cell problem were addressed in this investigation. The objective of this work was the development of a fuel cell electrode-catalyst for use in a carbon monoxide fuel cell, which would utilize polymer bound metal complexes as the catalytic species. Several commericially available polymers were examined to be used as backbones in the development of an electrode-catalyst. Polystyrene was chosen for more extensive study. The polymer was activated by complete or partial monochloromethylation of the pendant phenyls. Several schemes for binding cyclic tetradentate and bidentate ligands to the activated polymers were examined. Thin films were fabricated, but soluble ligand containing polymers were not obtained. The transition metals; cobalt and nickel were incorporated into the polymers, and these new materials were examined. In addition the electrochemical behavior of several metal complexes which hold potential as catalytic species was examined.

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CONTAINING POLYMERS AS FUEL
CELL CATALYSTS

FINAL REPORT

JAMES L. REED

15 June, 1987

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INTRODUCTION

One of the primary problems which has prevented the wide spread use of fuel cells has been the absence of a suitable electrode-catalyst for the electron transfer process. Carbon monoxide for many large scale and for extensive small scale applications is an ideal fuel cell fuel. Carbon monoxide can be generated from a wide variety of carbon sources, and combustion occurs under conditions which do not produce many of our most troublesome pollutants. It has therefore been proposed that polymer bound metal complexes be investigated as potential electrode-catalysts for a carbon monoxide fuel cell. The problems addressed in this investigation are; the chemical and electrochemical behavior of selected metal complexes in solution, physical properties of metal containing polymers, and the chemistry and electrochemistry of metal complexes.

A fuel cell is a device which converts chemical potential energy directly into electricity. Its function is therefore similar to that of a battery except in the case of a fuel cell fresh electroactive substance (the fuel) is constantly being supplied and spent material is being removed. In principle, the fuel for fuel cells need not be restricted to those substances commonly designated as fuels, but any pair of reactants which can be made to undergo an oxidation-reduction reaction may serve as fuel cell fuels. This not withstanding, economics will restrict fuel cell fuels for large scale or extensive small scale applications to the classes of substances now generally used as fuels. Thus the least expensive and most readily available oxidant is atmospheric oxygen. The reductant is any economically and environmentally viable substance which has favorable thermodynamics for oxidation by oxygen.

A principle difficulty in the implementation of fuel cell technology

has been the absence of suitable catalysts.   In many cases a reaction may

be spontaneous (favorable thermodynamics) and procede at a reasonable rate,

but when it is carried out in a electrolytic cell the mechanism is neces-

sarily different.   This often results in an unacceptably slow rate of

reaction.   The quest for a suitable catalyst is one which involves finding

a catalyst which will facilitate electron transfer between the fuel molecule

and the electrode surface.   In addition to favorable kinetics the catalyst-

electrode must have sufficient area such that transport to the catalytic

sites is not a severly limiting process, that is concentration polarization.

The elctrode must be able to pass large amount of current and thus must

have a low ohmic resistance. The carbon monoxide fuel cell using polymer

supported metal catalysts is an attractive candidate for study.

A general conceptual scheme for a polymer bound electrode catalyst is

shown below.

HOMOGENEOUS
PHASE
or
SOLID POLYMER
ELECTROLYTE

f_r

e^-

f_{ox}
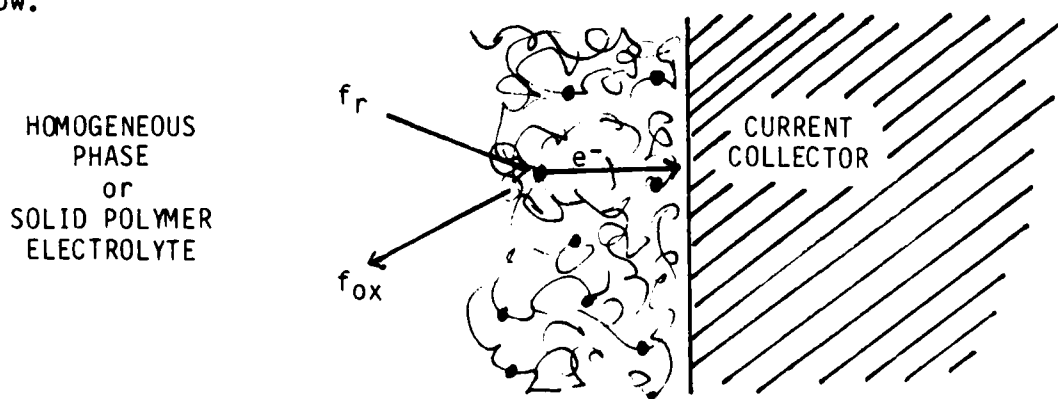
CURRENT
COLLECTOR

where f_r and f_{ox} are the reduced and oxidized forms of the fuel, respective_

ly.   The electrode catalysts, ∿ , are bound to the polymer which is in

intimate contact with the current collector.   In this, one of serveral

possible schemes, the catalyst is a solvent swollen film. If the partition

of the fuel between the homogeneous phase and the film favors the film,

concentration polarization may be avoided.   Electron transfer between the

catalyst molecule and the current collector may be effected by a number of

mechanisms.

ELECTRODECATALYST SYNTHESIS
AND
CHARACTERIZATION

Rationale

The synthetic objectives of the proposed research were to prepare organic polymers containing pendant Werner type metal complexes which are potential electron transfer catalysts, to fabricate the polymers into films and to prepare catalyst electrodes. The overall synthetic scheme is to activate commercial polymers in such a way as to make them reactive towards the multidentate ligands or their derivatives. The polymer backbones of interests are polyvinyl chloride, PVC, polyvinyl alcohol, PVA, and polystyrene, PS.

$$-\left(CH_2-CH\right)_n-$$
$$|$$
$$Cl$$
    PVC

$$-\left(CH_2-CH\right)_n-$$
$$|$$
$$OH$$
    PVA
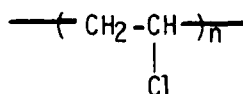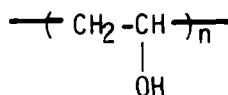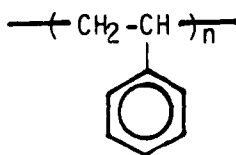
$$-\left(CH_2-CH\right)_n-$$
$$|$$
$$C_6H_5$$
    PS

Each of these polymers which are commerically available have unique characteristics which will variously effect the properties of an electrode catalyst. These three backbones will provide for the electrode-substrate interface, a range of polarities and solvation environments. Each of the polymer backbones must be activated by a different procedure. The activation schemes may be found below.

$$\mathrm{-\!\!+\!\!CH_2\!-\!CH\!\!\rightarrow_n} \ + \ \mathrm{mI^-} \ \longrightarrow \ \mathrm{-\!\!+\!\!CH_2\!-\!CH\!\!\rightarrow_m\!\!+\!\!CH_2\!-\!CH\!\!\rightarrow_{n-m}} \ + \ \mathrm{mCl^-}$$

with Cl on the first polymer, I and Cl on the products.

$$\mathrm{-\!\!+\!\!CH_2\!-\!CH\!\!\rightarrow_n} \ + \ \mathrm{mCl\!-\!SO_3\!-\!\langle\bigcirc\rangle\!-\!CH_3} \ \longrightarrow \ \mathrm{-\!\!+\!\!CH_2\!-\!CH\!\!\rightarrow_m\!\!+\!\!CH_3\!-\!CH\!\!\rightarrow} \ + \ \mathrm{mHCl}$$

with OH on the first, O–SO₃–C₆H₄–CH₃ and OH on the products.

$$\mathrm{-\!\!+\!\!CH_2\!-\!CH\!\!\rightarrow_n} \ + \ \mathrm{mCH_3OCH_2Cl} \ \longrightarrow \ \mathrm{-\!\!+\!\!CH_2\!-\!CH\!\!\rightarrow_m\!\!+\!\!CH_3\!-\!CH\!\!\rightarrow} \ + \ \mathrm{HOCH_3}$$

with phenyl on the first, and phenyl with CH₂Cl substituent and phenyl on the products.

The pendant ligand of primary interest is the tetradentate saturated macrocycle, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, tet. There exist two isomers for this ligand; the meso, tet-a, and the racemate, tet-b.
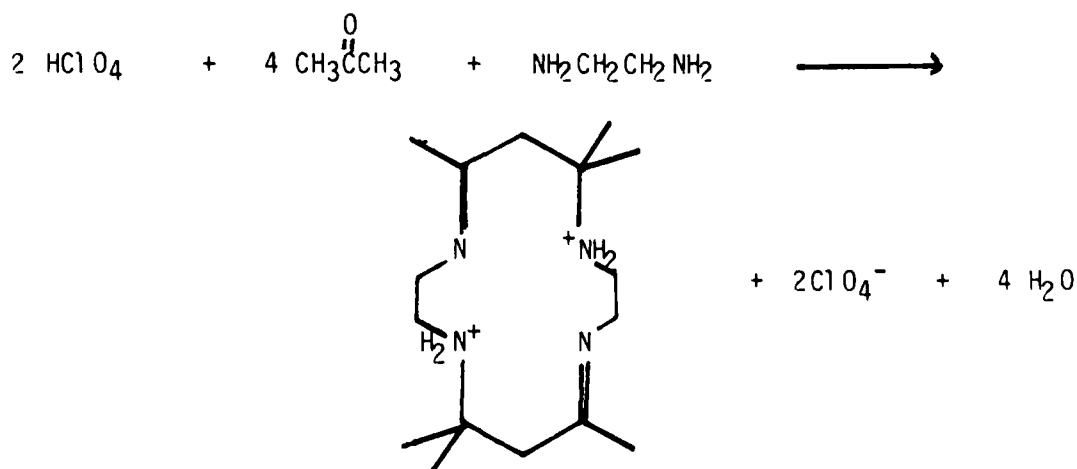

tet

If necessary other ligand systems will be considered, but the nitrogen macrocycle is preferred for several reasons. A nitrogen macrocycle was chosen because it strongly binds many metals. The macrocyclic structure is substi

tution inert in most cases, yet it leaves the 5 and 6 positions available for substitution by catalyst substrates. In addition a saturated macrocycle is relatively inert to oxidation-reduction reactions.

The nucleophillic amine nitrogens will then undergo reaction at the activated sites on the polymers yielding pendant amine polymers. This is followed by incorporation of metals into the pendant amine. The metals of interest for these studies are the first transition series elements. Film fabrication may be best carried out by subjecting the solid polymer to high temperatures and pressures, or by casting films from solutions of the polymer in a volatile solvent. The final stage involves the fabrication of polymer films which are insoluble in the media of interest. These films are then to be incorporated into a metallic electrode which would serve as a current collector in an operating cell.

5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane

The tet ligand is prepared by the condensation of acetone and ethylene diamin to yield a macrocyclic Schiffs base adduct

$$2 \ HClO_4 \quad + \quad 4 \ CH_3\overset{O}{\overset{\|}{C}}CH_3 \quad + \quad NH_2CH_2CH_2NH_2 \quad \longrightarrow$$

$$+ \quad 2ClO_4^- \quad + \quad 4 \ H_2O$$

The special solubility properties of the perchlorate salt of the desired product among the myriad of possible condensation products results in
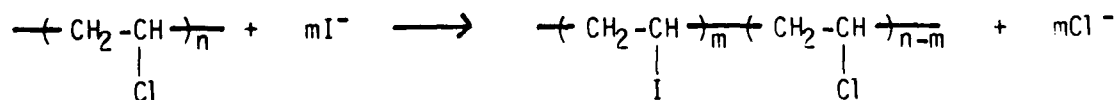
excellent yields of the cyclic amine. Reduction with sodium borohydride yields the desired macrocycle. Racemic and meso isomers were resolved by fractional crystalization.

Activation of Polyvinyl Alcohol

Activation of polyvinyl alcohol was accomplished by treatment of pyridine solutions of the polymer with p-toluenesulfonyl chloride. Polyvinyl alcohol (MW = 3,000 daltons) was tosylated in this manner. The NMR and IR spectra are consistent with the expected product. The NMR results were consistent with 100% conversion to tosylate. When, however, attempts were made to tosylate higher molecular weight polymers, solubility problems resulted in unacceptable products. Because of these problems the deveopment the of polyvinyl alcohol system was tabled for the time being.
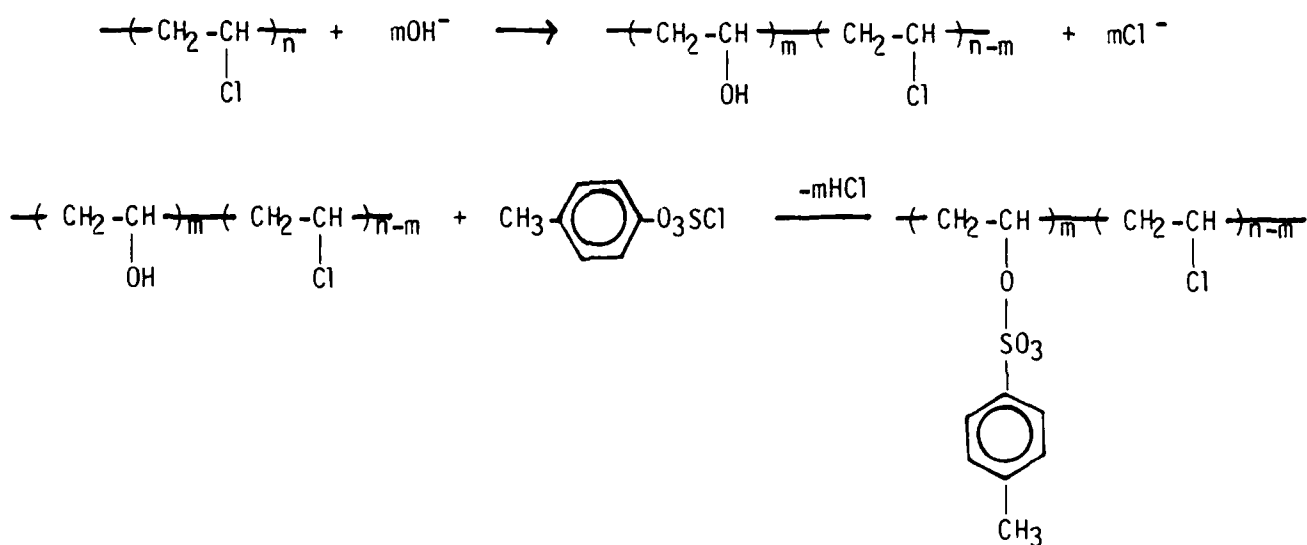
Activation of Polyvinyl Chloride

Several approaches to the activation of polyvinyl chloride might be envisioned. The first approach used was to replace some of the chlorides with iodide. Polyvinyl chloride was refluxed with $(CH_3CH_2)_4NI$ in tetrahydrofuran-methanol solutions. The molar ratio of chloride to iodide was usually around four.

$$-\!\!\left(CH_2-\underset{\underset{Cl}{|}}{CH}\right)_{\!n} + mI^- \longrightarrow -\!\!\left(CH_2-\underset{\underset{I}{|}}{CH}\right)_{\!m}\!\!\left(CH_2-\underset{\underset{Cl}{|}}{CH}\right)_{\!n-m} + mCl^-$$

The progress of the reaction was monitored by removing aliquots of the reaction mixture and precipitating the product with water. The filtrate is the analyzed for halogen. Using potentiometric titration both iodide and chloride could be determined. Typically after 24 hour reaction time the iodide concentration in the aliquot had decreased by 0.00316 mmole and the

chloride had increased to 0.0154 mmole. The observation that iodide had increased very little indicated little conversion had occurred. More importantly, however, the much larger increase in chloride suggests that there is a more rapid decomposition reaction effecting the polymer.

An alternative activitation scheme would involve hydrolysis of the parent polymer followed by tosylation of the hydroxyl groups.

$$\text{---}(\text{CH}_2\text{-CH})_n\text{---} + m\text{OH}^- \longrightarrow \text{---}(\text{CH}_2\text{-CH})_m(\text{CH}_2\text{-CH})_{n-m}\text{---} + m\text{Cl}^-$$

$$\text{---}(\text{CH}_2\text{-CH})_m(\text{CH}_2\text{-CH})_{n-m}\text{---} + \text{CH}_3\text{---}\langle\!\langle\bigcirc\rangle\!\rangle\text{---}\text{O}_3\text{SCl} \xrightarrow{-m\text{HCl}} \text{---}(\text{CH}_2\text{-CH})_m(\text{CH}_2\text{-CH})_{n-m}\text{---}$$

The hydroylsis reactions were carred out in tetrahydrofuran-1,4-dioxane mixtures, and KOH was the hydroxide ion source. The reaction was monitored by determination of the amount of chloride ion released. Typically after refluxing for 19 hours in 0.1 M base 19% of the chloride had hydrolyzed. The product was, however, an orange spongy solid and could not be used.

In the presence of a suitably strong nucleophile the chlorides on poly-vinyl chloride should undergo substitution without activation. In this case the base is activiated by treatment with lithium naphthalide to yield the very nucleophillic anion.

The nucleophile is then reacted with the polymer.
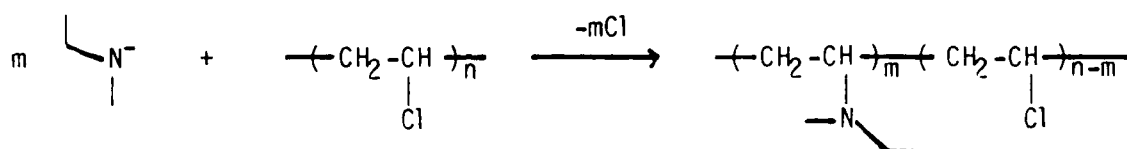
In reactions in which the anion of the base, in this case tet, was prepared in situ and reacted with polyvinyl chloride, there was evidence that amine incorporation had occurred. The products were, however, intractable solids and this approach was tabled.

Activation of Polystyrene

Of the three polymer matrices proposed above, polystyrene seems to be best suited for further study. The polyvinyl alcohols hold a great deal of promise particularly, because of the highly polar environments they would provide. For the studies described herein commercial polystyrene (Polysciences, Lot. No 0401) with a reported molecular weight of 30,000 daltons was used. The molecular weight distribution was determined using gel permeation chromatography. The column was calibrated against standard polystyrenes provided by the manufacturer and trichlorobenze was the solvent of choice (figure 1). The analysis revealed that the weight average molecular weight was 30,033 daltons, the number average molecular weight was 20,531 daltons and the z average molecular weight was 46,403 daltons. The dispersity was thus 1.464.

Polystyrene was activated by conversion to a benzychloride. Chloro-
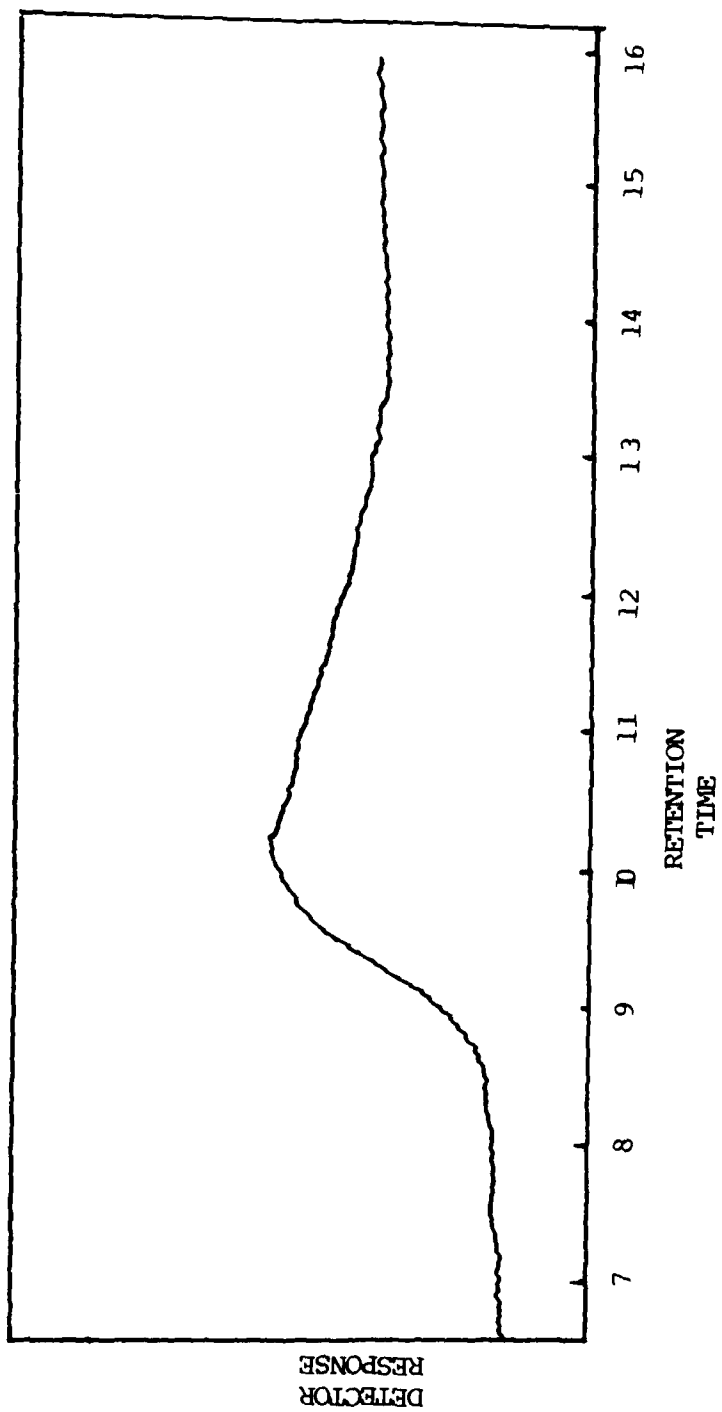
Gel permeation chromatogram of polystyrene, molecular weight 30,000 daltons.
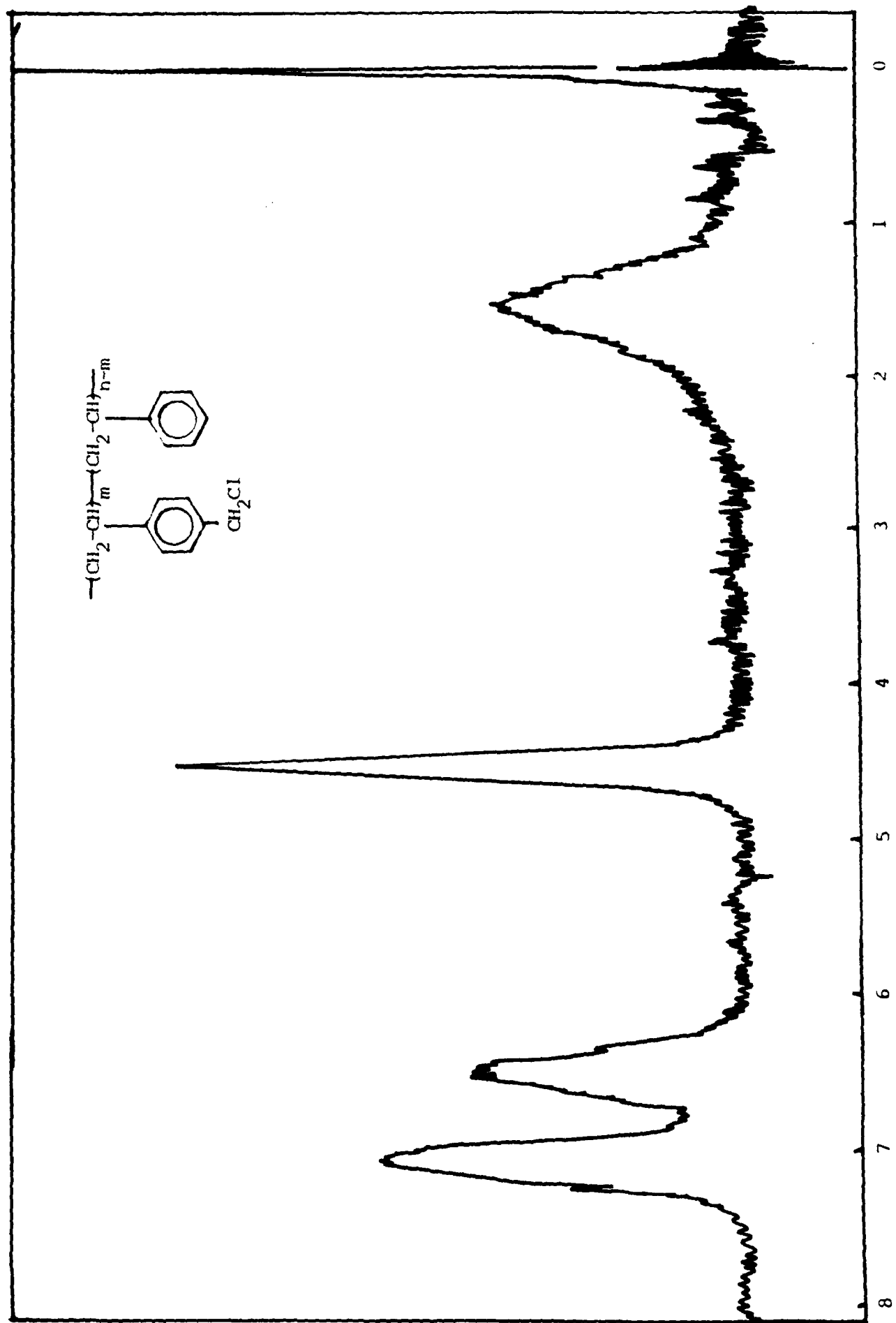
methylated polystyrene was prepared by chloromethylation of commercial polystyrene. In the earlier studies near 100% chloromethylation was attempted and chloromethylations in access of 99% were effected. Conversion, after several steps, of these polymers to metal containing polymers yields intractable materials with properties very different from those of the parent polymers. It was decided that it would be better to limit the chloromethylation to less than 35% of the phenyl rings. This would yield polymers with properties more akin to the parent polymer.

Chloromethylation was accomplished by treating commercial polystyrenes with chloromethylmethylether using a stannic or zinc chloride catalyst

$$+ \ CH_3OCH_2Cl \longrightarrow \qquad + \quad HOCH_3$$
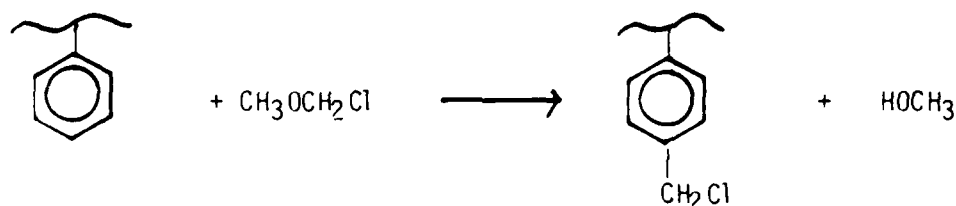
The products were characterized via infrared, and nuclear magnetic resonance as well as elemental analyses. The presence of the chloromethyl group was indicated by a band at $1265 cm^{-1}$ in the infrared and a peak at 4.5 ppm in the proton NMR. This was used semi-quantitatively to determined the extent of chloromethylation. A typical NMR is found in figure 2. In addition, the gel permeation chromatogramms of polystyrene and chloromethylated polystyrene are identical except for a shift in the moleculare weight (figure 3).

A more reactive benzylhalide may be obtained in for form of the benzyl-iodide. The chloromethyl polystyrene may be converted to the iodomethyl polystyrene by treating the chloride with an iodide salt. The reaction is driven to completion by precipitation of the less soluble sodium chloride

Nuclear Magnetic Resonance Spectrum of Chloromethylated Polystyrene

$$-(CH_2-CH)_m-(CH_2-CH)_{n-m}-$$

with phenyl groups; CH_2Cl substituent

11
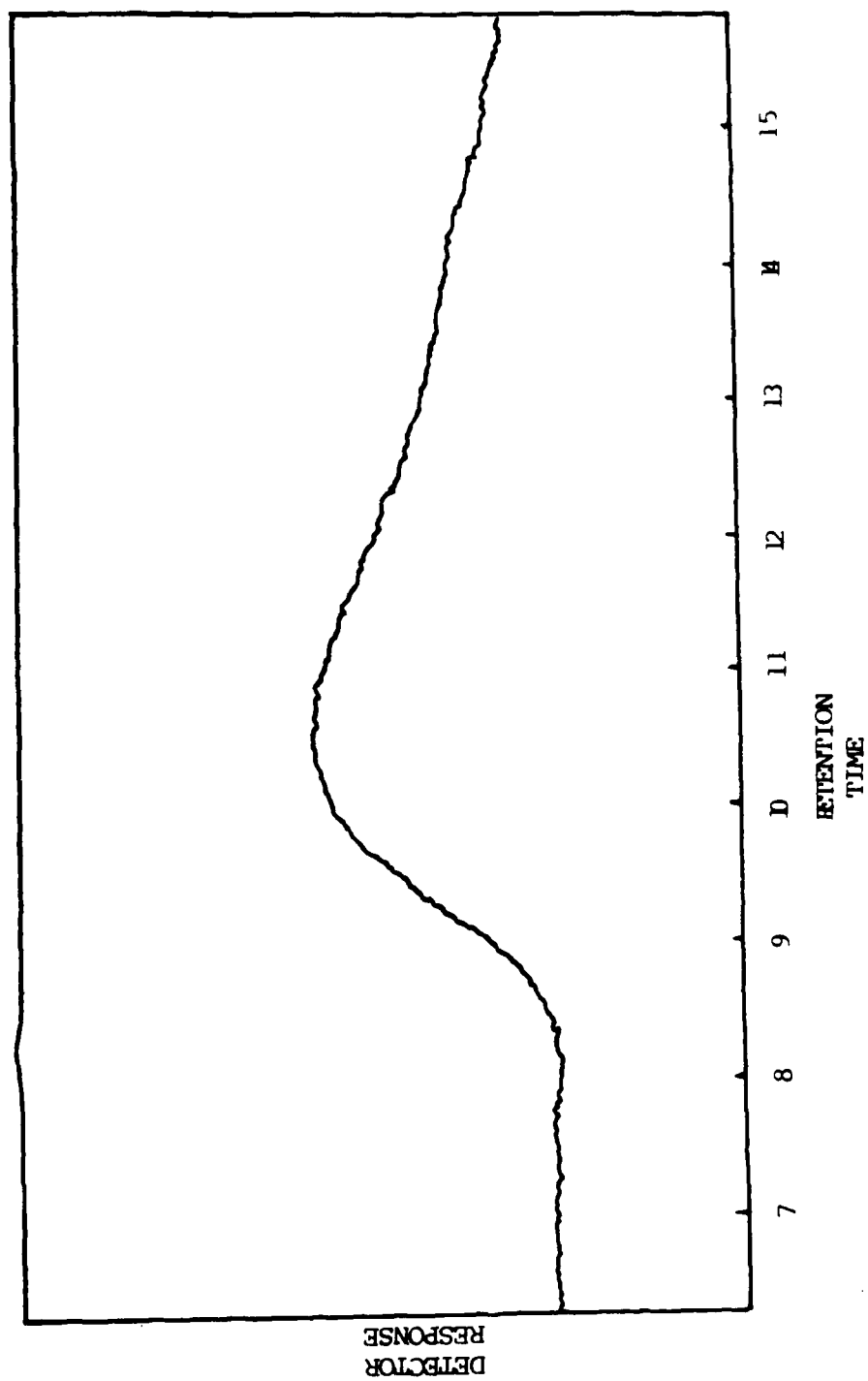
Gel permeation chromatogram of chloromethylated polystyrene, parent polymer molecular weight 30,000 daltons.

Appreciable yellowing of tne polymer occurred during the reaction, and an insoluole material was thus ootained. The likely source of tne problem was tne presence of oxygen in the system which would yield radicals and thus yield radical initiated polymer reactions and discoloration. It was feared that because the tet-a and tet-b both occur as hydrates, they would not be sufficiently nucleophillic to be reactive towards the chloride. As the studies described below indicate, this is not the case. As a result the iodination route was not further pursued.
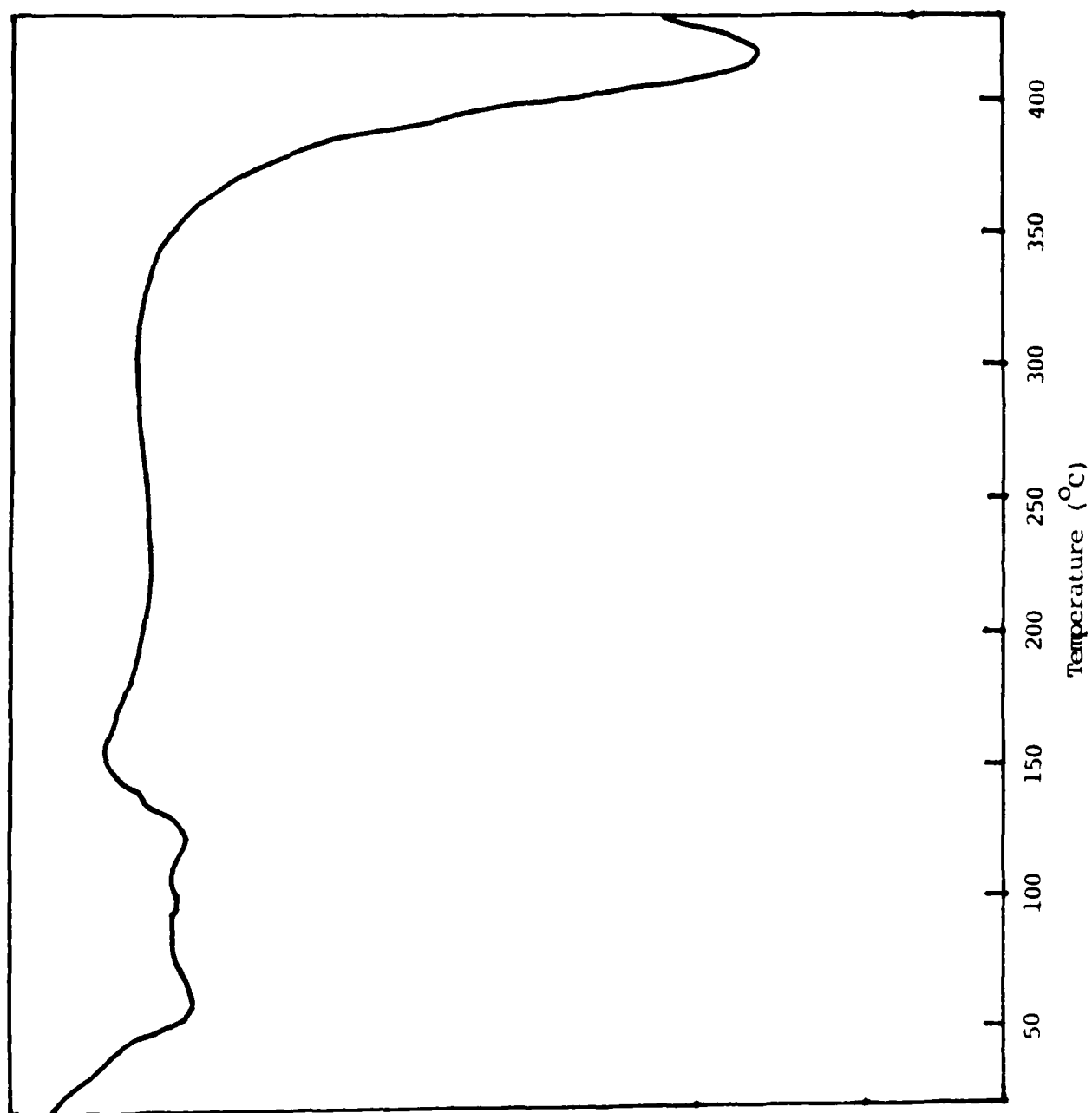
Reaction of Chloromethylated Polystyrene and Tet

Because benzyl chlorides undergo facile substitution, the cyclic tetraamine is expected to add to the chloromethylated polymer under mild conditions by the reaction
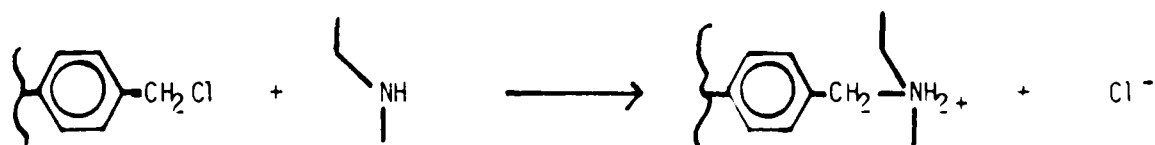
In order to access and understand this reactivity, the reaction was studied calorimetrically. Solid mixtures of the chloromethylated polymer (from the 30,000 dalton polystyrene) and the tetraamine were prepared either by mechanical mixing and grinding to a fine powder, or by dissolving them in tetrahydrofuran, evaporating the solvent and grinding the resultant film to a fine powder. Differential scanning calorimetric scans were performed on weighed samples. Scans of sulfur samples were performed before and after the samples were run for calibration purposes.

Scans of chloromethylpolystyrene (15% chloromethylated, from 30,000 molecular weight polystyrene) showed no transitions below 54°C (figure 4).

14

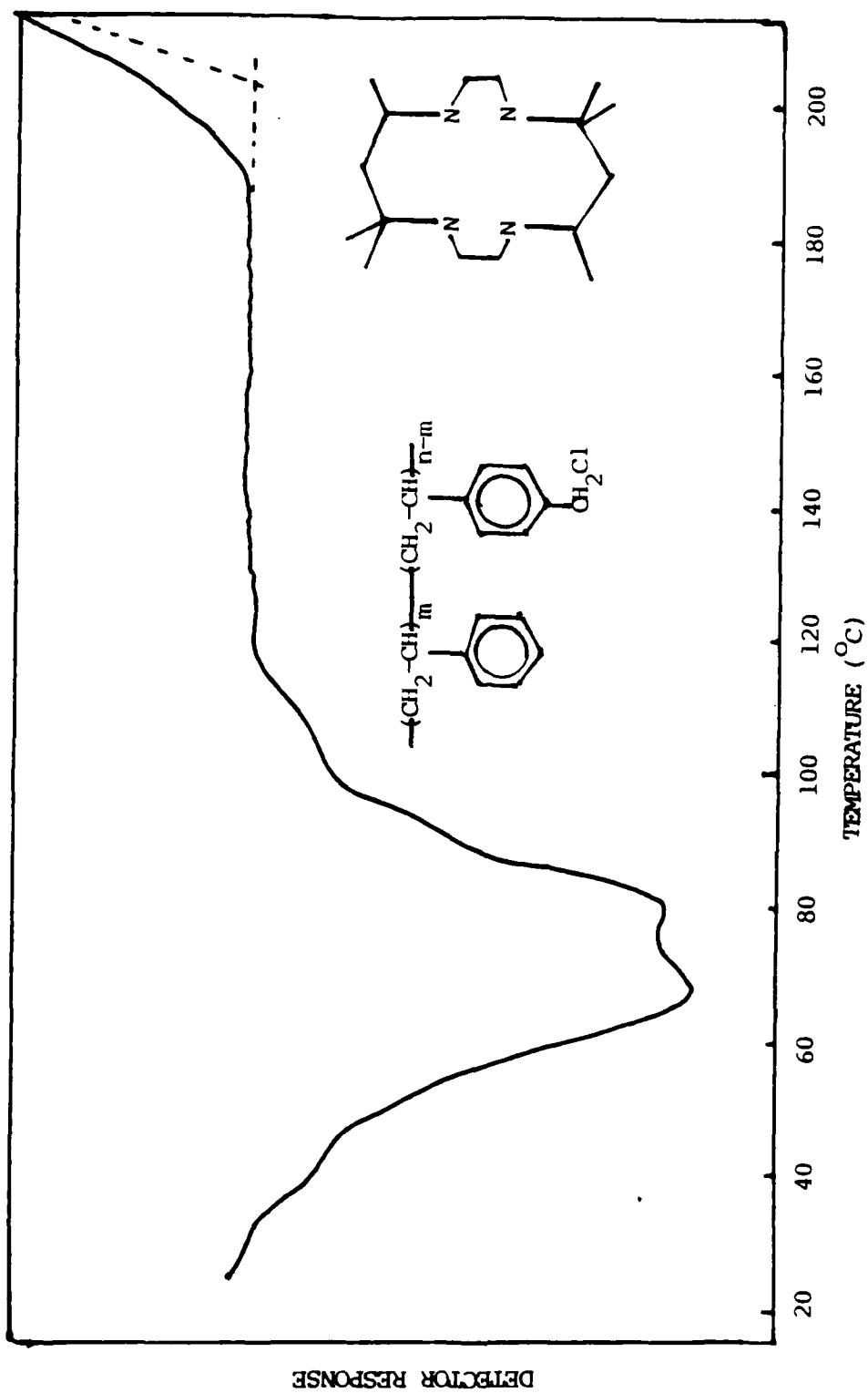Differential scanning calorimetry for chloromethylated polystyrene.

A second order transition was observed at 54°C. Scans of tet-b which was a hydrate showed endothermic first order transitions at 54.4°C with an enthalpy of 4.27 kcal/mole and 109°C with an enthalpy of 2.5 kcal/mole (figure 5). The latter transition coincides with the observed melting of the compound. Scans of the physical mixture of chloromethylated polystyrene and tet-a in which the amine was in molar excess of the chloromethyl groups show an endotherm at 48.0°C (18.65 kcal/mole of amine or 48.42 kcal/mole of-CH_2Cl) and a large exotherm at 199°C (figure 6). The scans of mixtures formed by dissolving the components in tetrahydrofuran show similar results.

Studies were also carried out using the same mixture suspended in N,N-dimethylformamide (45% (w/w)). These scans were complicated bacause dissolution of the solids is also occurring during the scan. These results are difficult to interpret. It does appear, however, that at fairly low temperatures the chloromethylated polymer and the amine undergo an endothermic reaction as does the mixture of the solids. Although the endothern occurs very near that of the first tet-a transition, the enthalphy is four times that of tet-a alone. The coincidence of the endotherm with that of tet-a is not unexpected since a phase transition of some sort would be necessary to effect mixing. These observations are supportive of the possibility of forming films from the melt reactions between the solids, and between the components in solution at moderate temperatures.

The solution reactivity of chloromethylpolystyrene and tet-a was studied in refluxing 1,4-dioxane. The proportions used correspond to a two fold excess of chloromethyl groups over macrocycle. Periodically aliquots

Differential scanning calorimetry of tet-b
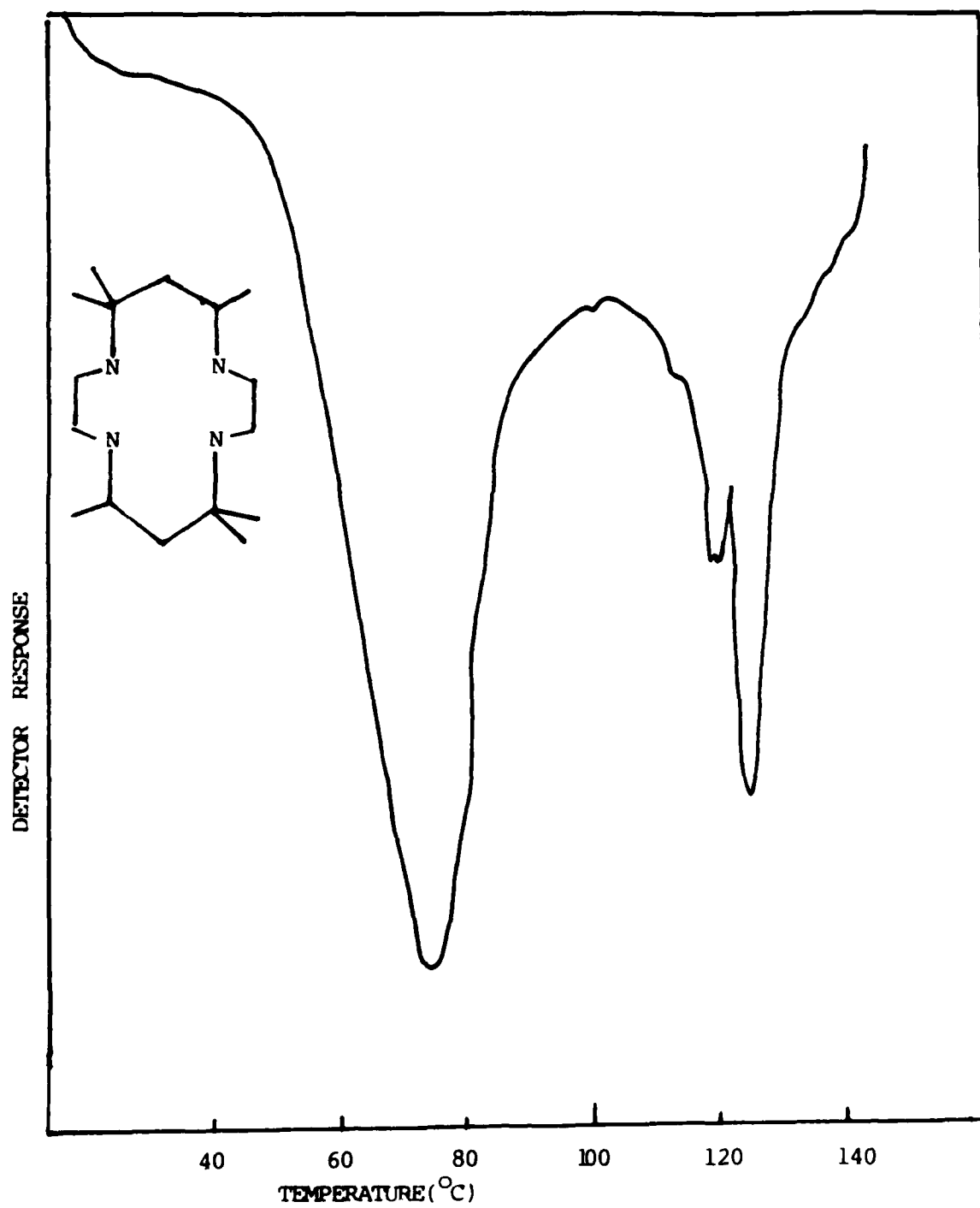
Differential scanning calorimetry of a dry mixture of chloromethylated polystyrene and tet-b

were removed and the amount of hydrogen ion liberated was determined via acid-base titation (figure 7). It thus appears that the reaction of one mole of halogen with one mole of macrocyle is facile under these conditions, and is essentially complete after two hours. The infrared spectrum of the product show bands assignable to both the parent polymer and the macrocycle. The product could be titrated to determine the degree of amine incorporation. The product was insoluble in all common solvents and formed gels in most.

Because tet is a tetraamine, a single macrocycle may react with one or more than one chloromethyl group. This will result in the formation of crosslinks between chains within the polymer. The morphological effect of polymer crosslinks is the formation of gels. Gel formation prior to processing and fabrication is undesirable because of the difficulty in characterizing the materials as well as in the fabrication of the polymers to form, in our case, films. It is therefore desirable to avoid gel formation prior to the final fabrication step. Reactions of the tet-a and chloromethylated polystyrene in equimolar amounts of tetraamine and chloromethyl groups did in fact yield gels.

To study the extent of gel formation tet-a was reacted with chloromethyl polystyrene under conditions in which there was a five fold excess of the tetraamine over the chloromethyl groups. As the reaction proceeded the percent of the polymer product which was gel was determined. It should be noted that once all of the chloromethyl groups have reacted, gel formation is not possible by this mechanism, therefore an excess of the amine should retard gel formation.
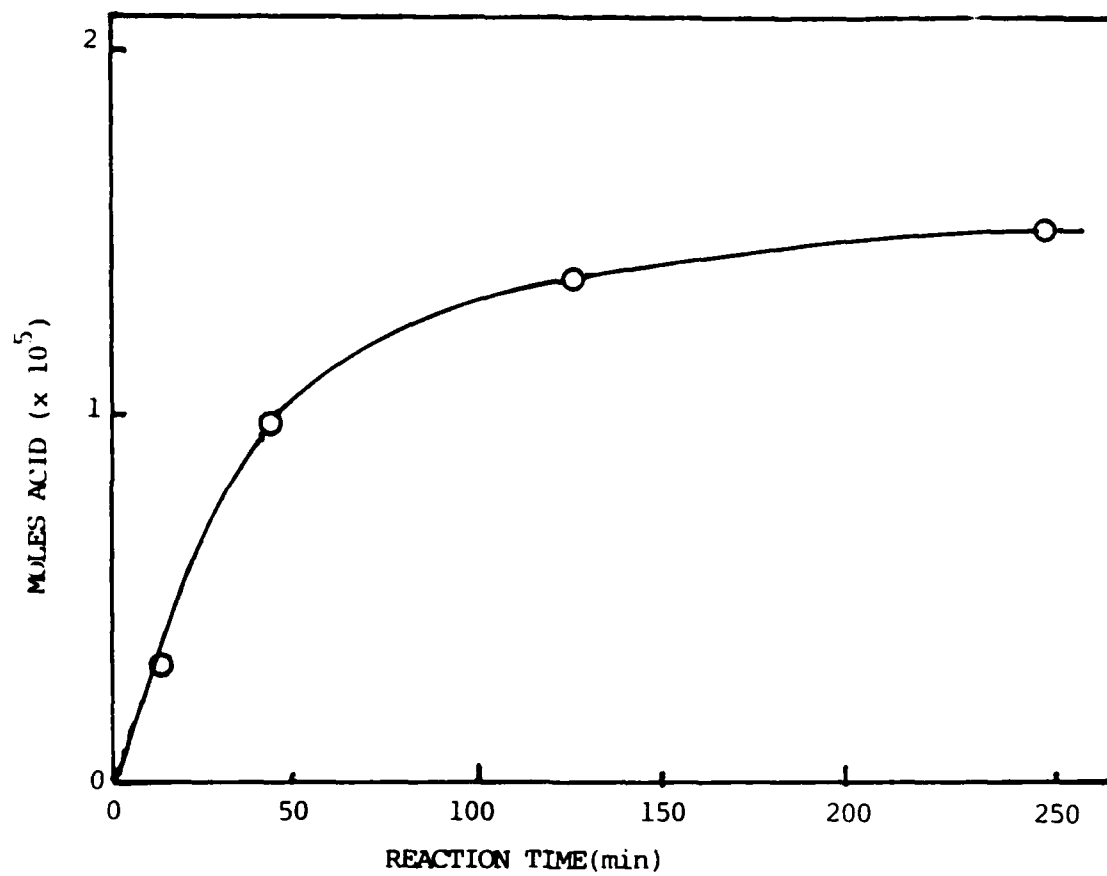
Hydrogen ion liberated during the reaction of excess
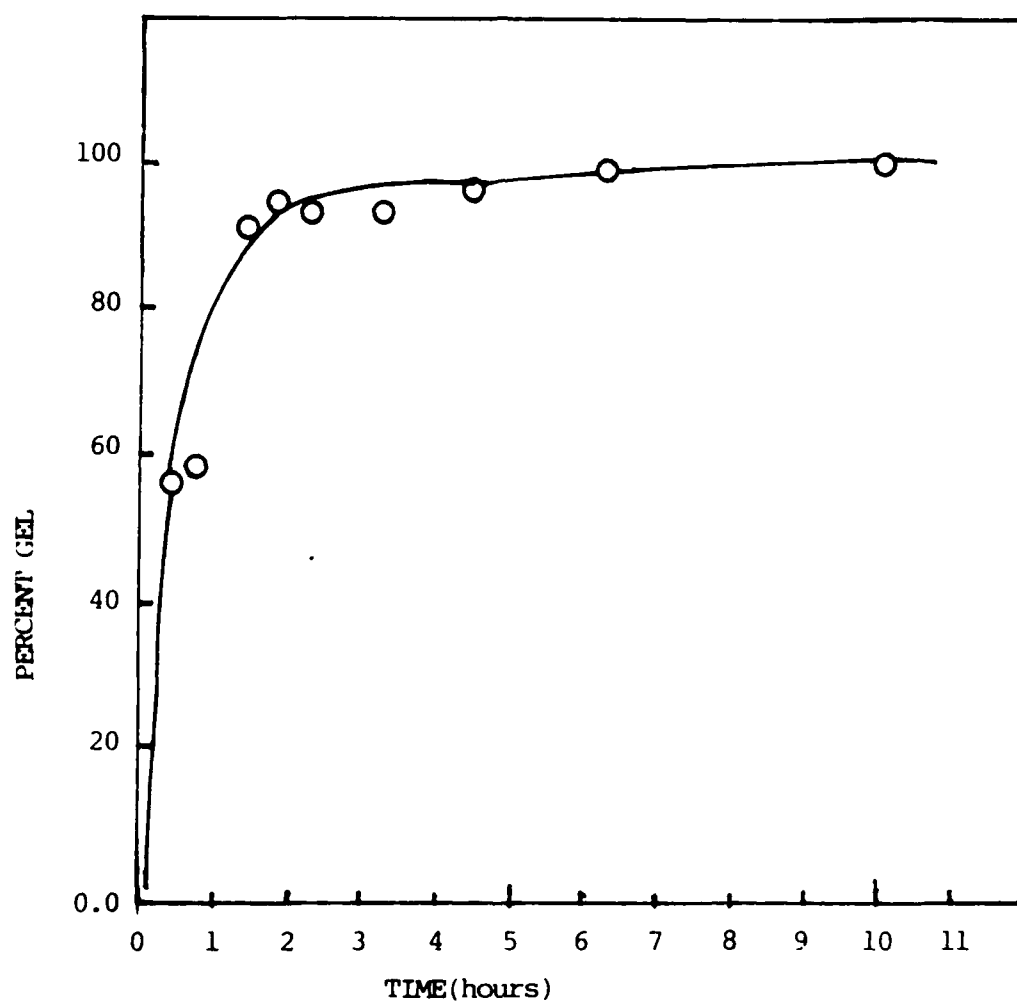tet-b with chloromethyl polystyrene.

TABLE

Sample	Reaction Time (hours)	Percent Gel
1	0.33	57
2	0.62	59
3	1.38	92
4	1.77	95
5	2.25	93
6	3.25	93
7	4.75	94
8	6.25	100
9	10.43	100

The percent gel formated for various reaction times for the reaction of tet-a with chloromethylated polystyrene.
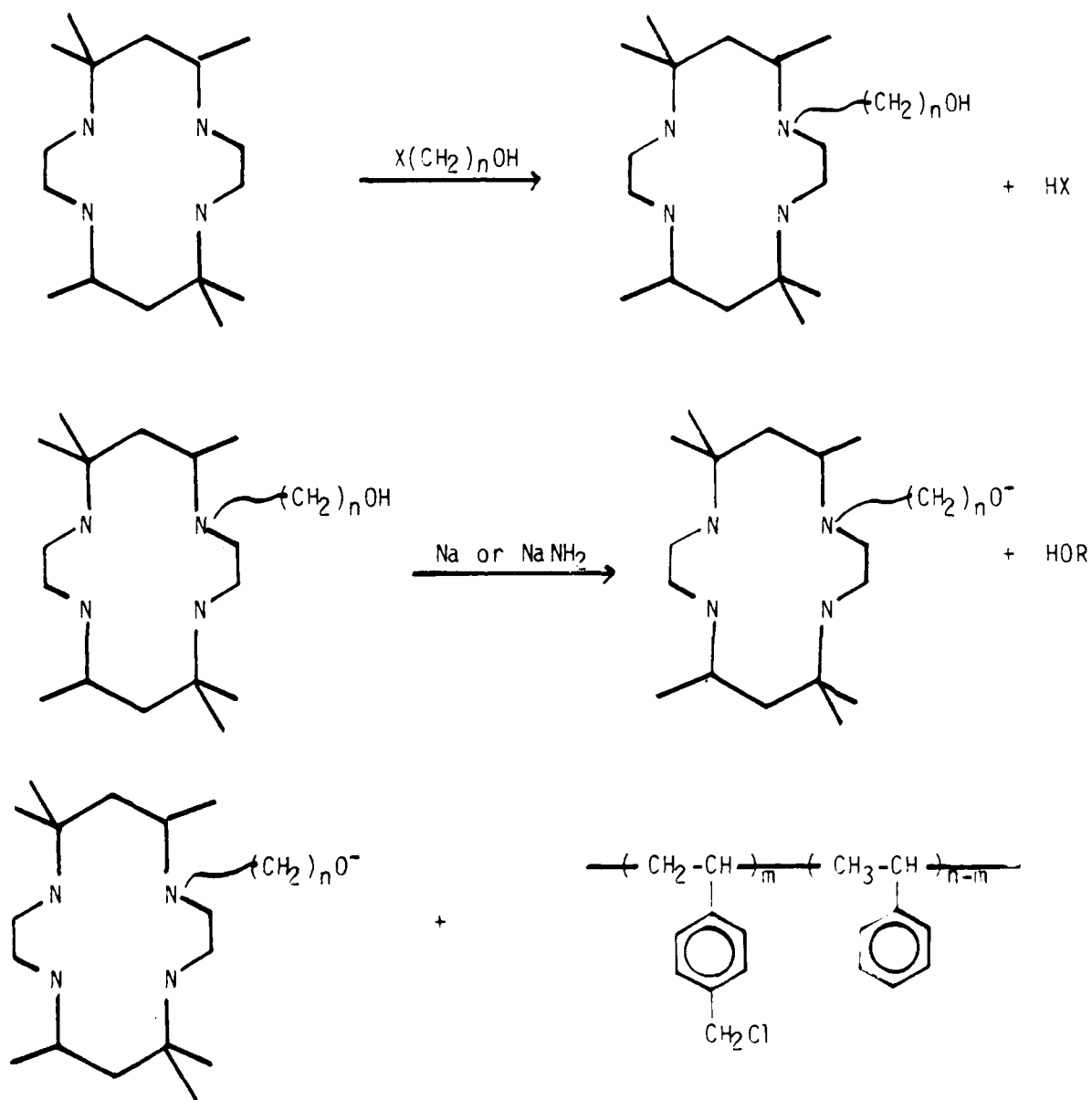
In refluxing tetrahydrofuran which was 0.46 M in tet-a and 0.092 M in chloromethyl groups on the polystyrene yielded 50% gelled polymer after a reaction time of only one-half hour. Essentially all of the polymer present was gelled after two hours. It appears that even under conditions which should surpress gel formation, extensive gellation occurs (figure 8). In a model reaction tet-a was reacted with a two fold excess of benzylchloride. The product was isolated in good yield. Analysis revealed that tet-a did in fact undergo facile reaction with benyzlchloride.
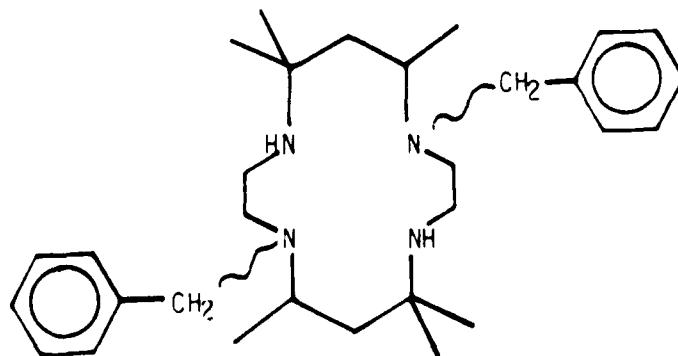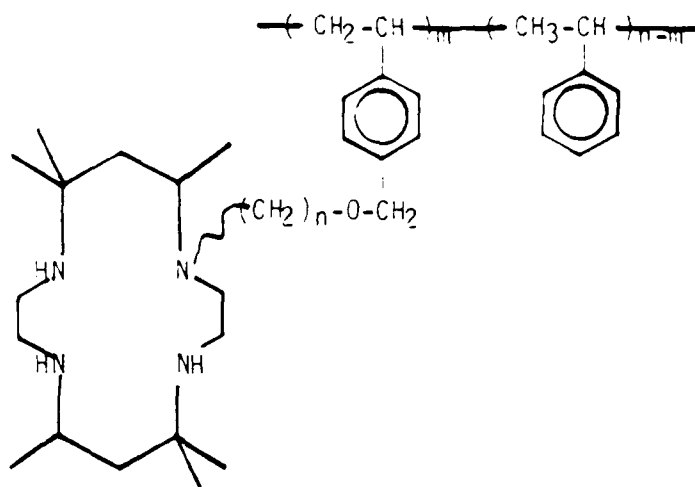
A plot of the percent gel versus reaction time for
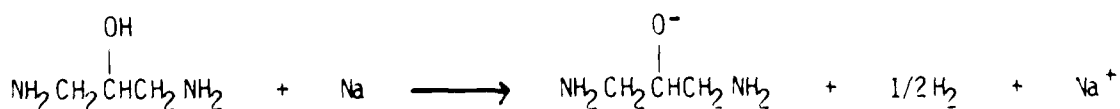the reaction of chloromethyl polystrene with tet-b.

In that the direct reaction of the tetraamine with the chloromethylated polymer yielded primarily gels, alternative routes to the preparation of polymers containing the pendant tetraamine were sought. The procedure is underdevelopment. The systhetic scheme is given below.

$$\text{(tetraamine macrocycle)} \xrightarrow{\ X(CH_2)_nOH\ } \text{(macrocycle)}-(CH_2)_nOH \quad + \quad HX$$

$$\text{(macrocycle)}-(CH_2)_nOH \xrightarrow{\ Na\ or\ NaNH_2\ } \text{(macrocycle)}-(CH_2)_nO^- \quad + \quad HOR$$

$$\text{(macrocycle)}-(CH_2)_nO^- \quad + \quad \left[-CH_2-CH \right]_m \left[CH_3-CH \right]_{n-m}$$
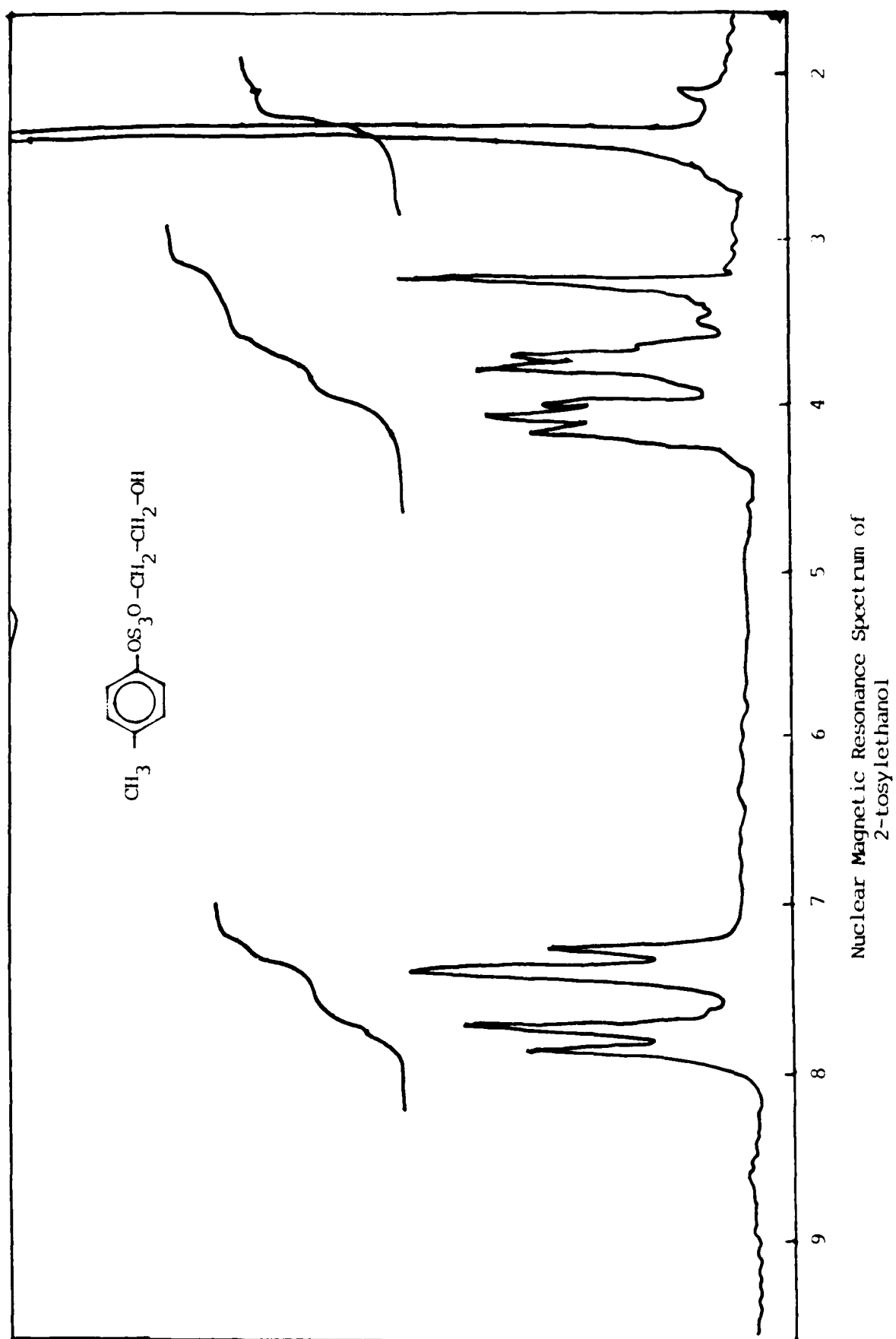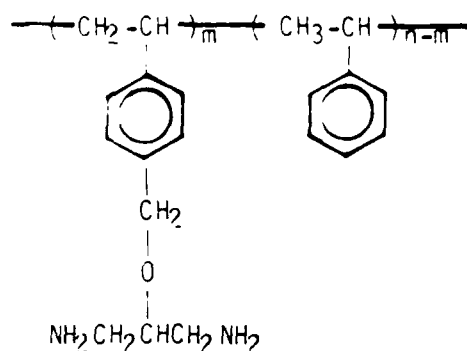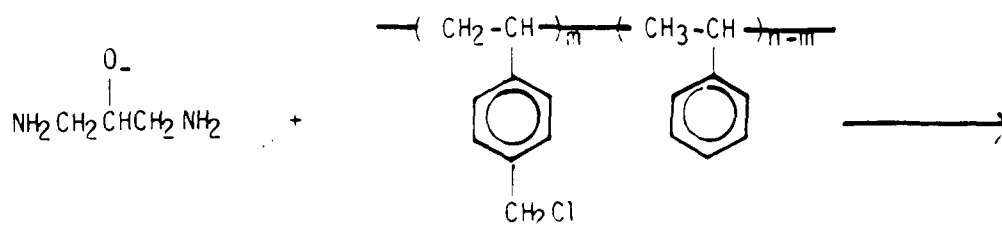
with pendant phenyl groups, one bearing CH_2Cl.

where x = Br or toslyate and n = 2 or 3. The 2-hyrdroxyethyl toluene-p-sulfonate and the 3-bromopropan-1-ol were chosen for study. The tosylate was prepared by the reaction of para-toluene sulfonylchloride with excess ethylene glycol. Although some difficulty was encountered in preventing the formation of the ditosylate, excellent yield of the desired product was obtained (figure 9). The 3-bromopropan-1-ol was purchased commercially. The reactions of these with tet-a and tet-b are currently under investigation.

The reactions described in the previous paragraphs result in the formation of amine alcohols. These may be converted to the corresponding alkoxides by treatment with sodium or sodium amide. The reaction of 1,3-diaminopropan-2-ol with sodium and sodium amide to yield the corresponding alkoxides in solution was carried out. The alkoxides were then reacted in situ with chloromethyl polystyrene. Excellent yields of the expected diamine were obtained.

24

Nuclear Magnetic Resonance Spectrum of
2-tosylethanol

$$NH_2CH_2\overset{\overset{O^-}{|}}{C}HCH_2NH_2 \quad + \quad -\!\!\left(\!CH_2\!-\!\underset{\underset{CH_2Cl}{\big|}}{\overset{}{C}}H\!\right)_{\!m}\!\!\left(\!CH_3\!-\!CH\!\right)_{\!n-m} \quad \longrightarrow$$

$$-\!\!\left(\!CH_2\!-\!CH\!\right)_{\!m}\!\!\left(\!CH_3\!-\!CH\!\right)_{\!n-m}$$

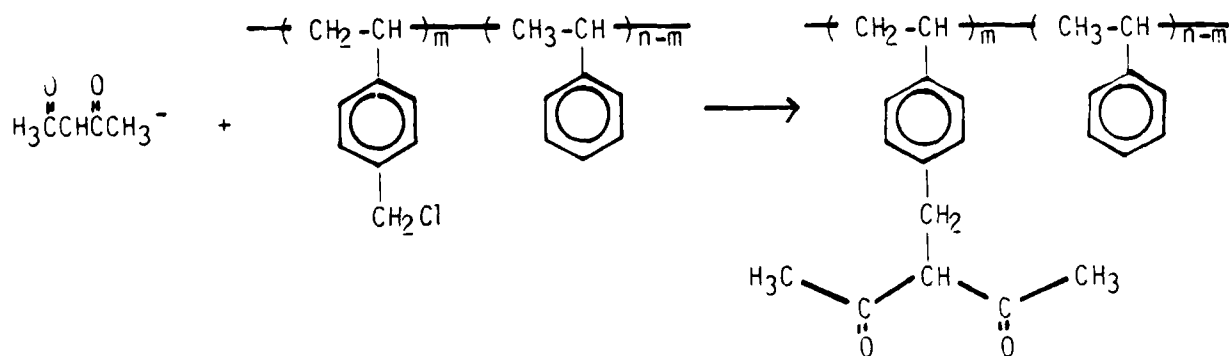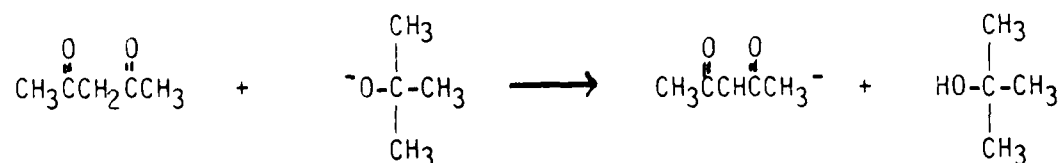with pendant: $CH_2\!-\!O\!-\!NH_2CH_2CHCH_2NH_2$

The extent of amine incorporation was determined quantitatively by acid-base titration.

The 2,4-pentanedionate ion was preopared by treatment of 2,4-pentane-dione with potassium tertiary butoxide

$$CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}CH_3 \quad + \quad -O\!-\!\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\!-\!CH_3 \quad \longrightarrow \quad CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}HCCH_3{}^{-} \quad + \quad HO\!-\!\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\!-\!CH_3$$

$$H_3\overset{\overset{O}{\|}}{C}C\overset{\overset{O}{\|}}{C}HCCH_3{}^{-} \quad + \quad -\!\!\left(\!CH_2\!-\!\underset{\underset{CH_2Cl}{\big|}}{\overset{}{C}}H\!\right)_{\!m}\!\!\left(\!CH_3\!-\!CH\!\right)_{\!n-m} \quad \longrightarrow \quad -\!\!\left(\!CH_2\!-\!CH\!\right)_{\!m}\!\!\left(\!CH_3\!-\!CH\!\right)_{\!n-m}$$

with pendant: $CH_2\!-\!CH$ bearing $H_3C\overset{\overset{}{C}}{\underset{\underset{O}{\|}}{}}\text{—CH—}\overset{}{C}\underset{\underset{O}{\|}}{}CH_3$

This was reacted with chloromethyl polystyrene to yield a diketone containing polymer. These latter two polymers are particularly interesting in that they pose an alternative to preparing nitrogen macrocyclic ligands by Scniffs base condensation. The derivatization using preformed tet have thus far yielded only gels rather than soluble polymers.

Metal Containing Polymers

Highly loaded metal containing polymers were prepared from polystyrenes which were completely converted to chloromethyl polystyrene and the lithium naphthalide method for preparing amine containing polymers was used. Pendant tetraamine polymers are converted to cobalt tetraamine polymers by refluxing the swollen polymers with anhydrous cobaltous chloride in tetrahydrofuran. The product is a green-brown powder. The expected repeat unit in the polymer is

$[Co(\underline{PS}\text{-tet-h})]^{2+}$
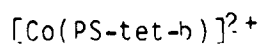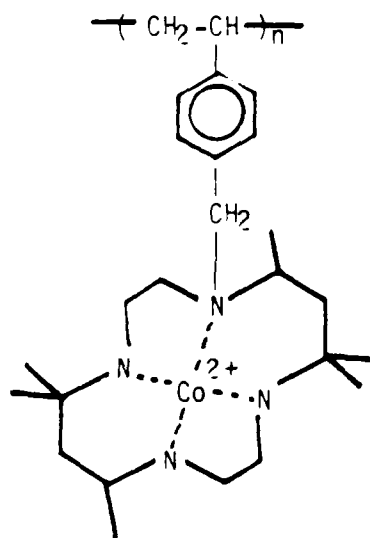
which would contain 10.5% cobalt. The product was found to contain 11.1% cobalt. The powder was then extracted for 24 hours with tetrahydrofuran, dried and analyzed for cobalt. The polymer after extraction contained 11.7% cobalt. The increase in cobalt is most likely the result of the extraction organic material from the polymer. In both cases the cobalt content exceeded the theoretical. This suggests that species such as that shown below might be present in the polymer
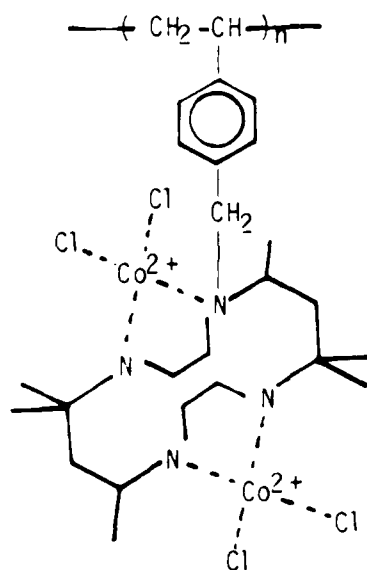
Whereas extraction with tetrahydrofuran did not result in loss of cobalt, treatment with concentrated solutions of LiBr or NH_4SCN did extract cobalt. This observation is indicative of two things. Structures such as those shown above would be easily decomposed by excess halide or psuedohalide. The form of cobalt in the polymer must be cobalt(II) since trivalent cobalt would be inert to substitution.

The polymers with heavy metal loadings were intractable and did not seem to be suitable for our application, work was discontinued in this area. Rather work was concentrated on polymers in which less than thirty

percent of the phenyl rings are substituted.

Polystyrene Derived Films

Polymer films were prepared by curing solutions of tet-b with chloro-methylated polystyrene in N,N-dimethylformamide at 90°C. At the end of the curing period all of the solvent had evaporated yielding a pale yellow film ($0.009g/cm^2$). This film was insoluble in all common organic solvents and after extensive extraction the mass of the film was reduced from that of the starting materials by only 4.5%. Both starting materials were very soluble in the extraction solvents. The number of chloromethyl groups in the polymer exceeded the amount of tet-b added, and it is expected that 21% of phenyls should have pendant tet-b.

The curing reaction was expected to give rise to two types of product structures.
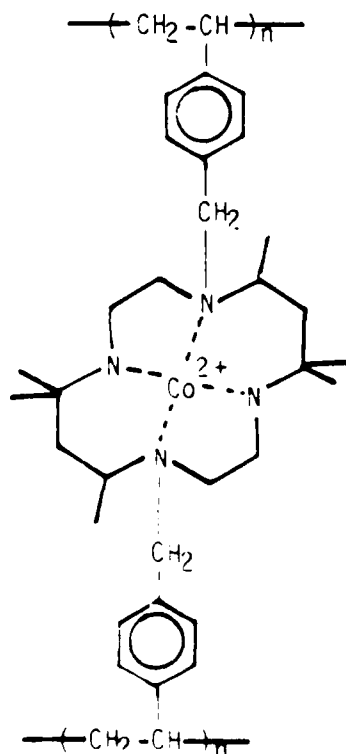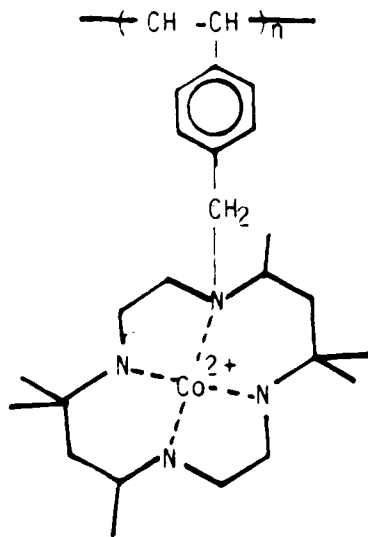
The latter structure constitutes crosslinks within the polymer network. These would result in the formation of gels and insoluable materials.

Cobalt was incorporated into the film by refluxing the film with excess annydrous cobaltous chloride in tetrahydrofuran. The film metallated by this procedure contained 3.11% cobalt. The film was deep blue-green and transparent. The optical spectrum was recorded and contained a flat broad band from 730 to 560nm and a gradual increase in absorption below 440nm (figure 10). The broad non-guassian shape of this band is indicative of the presence of more than one absorbing species in the film. Since the presence of amine ligands shift the electrode potential for the Co(III)/ Co(II) couple in favor of cobalt(III), and since the metal incorporation reaction is carried out in air and in the absence of water the expected reaction product is
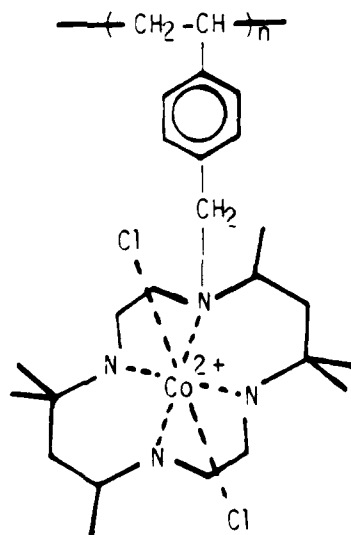
The spectrum of $[Co(tet-b)Cl_2]^+$ was recorded in the solid state and a band was observed at 626nm and a shoulder at 469nm (figure 11). The absorption minimum was at 537nm. The observed spectrum of the film would be consistent
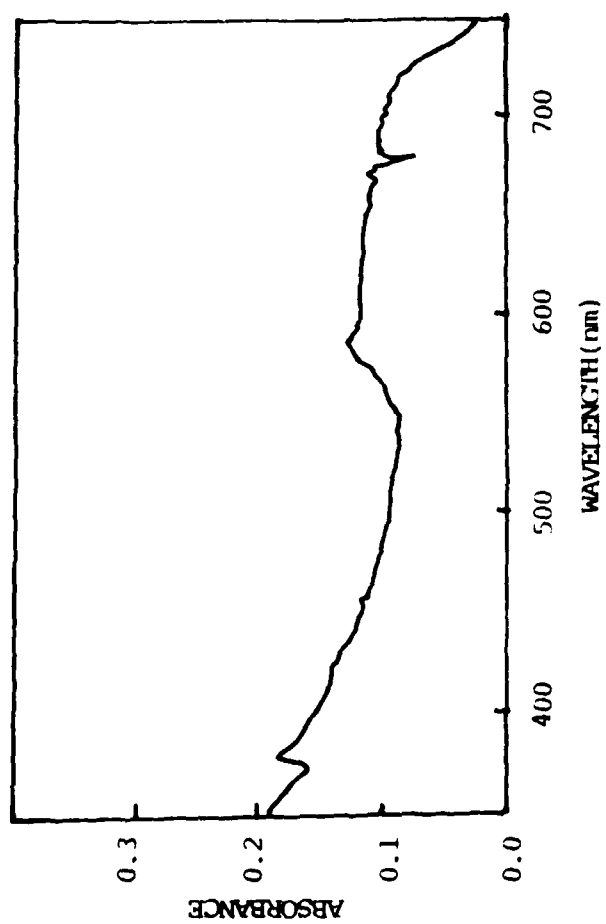
Optical spectrum of cobalt containing film.
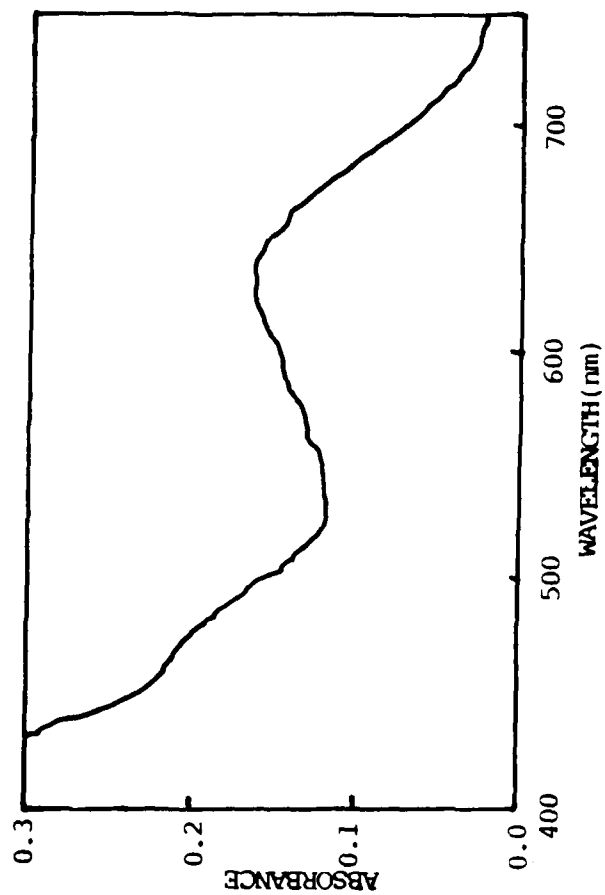
Optical spectrum of solid $[Co(tet-b)Cl_2]ClO_4$.
Average of two scans.

32
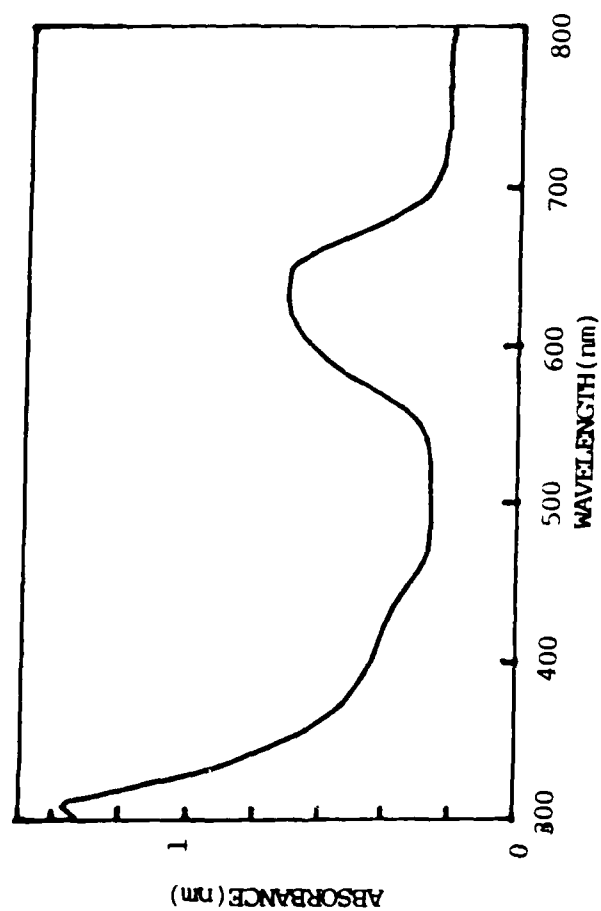
Optical spectrum of cobalt containing film after
extraction with thiocyanate solution.

with the presence of $[Co(tet-b)Cl_2]^+$ but absorptions extending to 700 nm is indicative of the presence other species.

In that cobalt(III) amine complexes are unlikely to have band maxima as low as 700nm a cobalt(II) species is indicated. Because cobalt(II) is kinetically labile, and has a preference for soft ligands, the film was treated with a N,N-dimethylformamide NH_4SCN solution for two days at room temperature. The solution became blue-green which is indicative of the $Co(SCN)_4^{2-}$ ion. The film was then extracted with N,N-dimethylformamide then with tetrahydrofuran. The film was blue green. The fact that cobalt could be extracted from the film supports the proposed presence of cobalt(II) in the polymer, and the retention of the blue-green color in the film supports the presence of a cobalt(III) species in the polymer. The spectrum of the film was recorded once more. It contained a band at 624nm with a shoulder at 583nm (width at half height of 2.9kK) and evidence of a shoulder at 403nm. (figure 12). This spectrum would be consistent with the presence of $[Co(\underline{PS}-tet-b)(SCN)_2]^+$ or $[Co(\underline{PS}-tet-b)Cl_2]^+$ in the polymer film.

Cobatous Ion Spectra

To assist in interpreting the optical spectra of cobalt containing films, the spectra of several cobaltous species in tetrahydrofuran were studied. A 0.0521 M cobaltous chloride solution was prepared. The $CoCl_4^{2-}$ ion was prepared in situ by making the solution .30 M in LiCl. Similarly $CoBr_4^{2-}$ ion was prepared in situ by making the solution 0.20 M in LiBr. Attempts to prepare $Co(NCS)_4^{2-}$ failed due to low solubility of thiocyanate salts and precipitation of reaction products. The addition of triethylene-tetraamine also caused precipitation of the product.

The spectra of both $CoCl_4^{2-}$ and $CoBr_4^{2-}$ had moderately intense bands

in the 700nm region (figures 13b and 13c). The spectrum of $CoCl_2$ was very probably of the CoCl $^-$ ion formed in organic media. The presence of absorp tions at 700nm in the cobalt containing films su bound cobalt species which should be cationic may have a tetrachloroco- baltate counter ion. Thus the metal incorporation reaction might be more accurately represented as

$$2CoCl_2 + \underline{PS\text{-}tet\text{-}b} \qquad [Co(\underline{PS\text{-}tet\text{-}b})]^{2+} + CoCl_4^{2-}$$
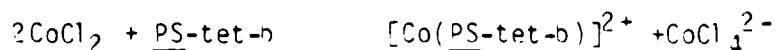
This may be followed by air oxidation of the cobalt amine. This proposal would be consistent with the high cobalt analyses obtained for some polymer films for which cobalt was not leached by extensive washing and extraction. On the other hand cobalt(II) was easily leached from the polymer if excess chloride, bromide or thiocyanate ions were present in the film.

Nickel Containing Films

Nickel containing films were also prepared. They were prepared in the same manner as the cobalt films. The nickel salt used was the hydrous nickel acetate, and it was reacted with the tet-b containing polymer film. Metal incorportation was in evidence by the color of the product films. The optical spectrum contained a broad band centered at 720 nm and a shoulder at 460 nm (figure 14). The latter may be indicative of the Ni(tet-b)$^{2+}$ ion. The infrared spectrum exhibited an strong absorption at 1745 cm^{-1} which was assigned to an acetate counter ion. Repeated treatment of the films with tetraflouroboric acid did not result in the elimination of this band, but it did result in the 460 nm absorbance in the optical spec- trum becoming more prominent. The stereochemistry of nickel(II) is complex, and it was therefore difficult to either identify or carry out reactions on the films.
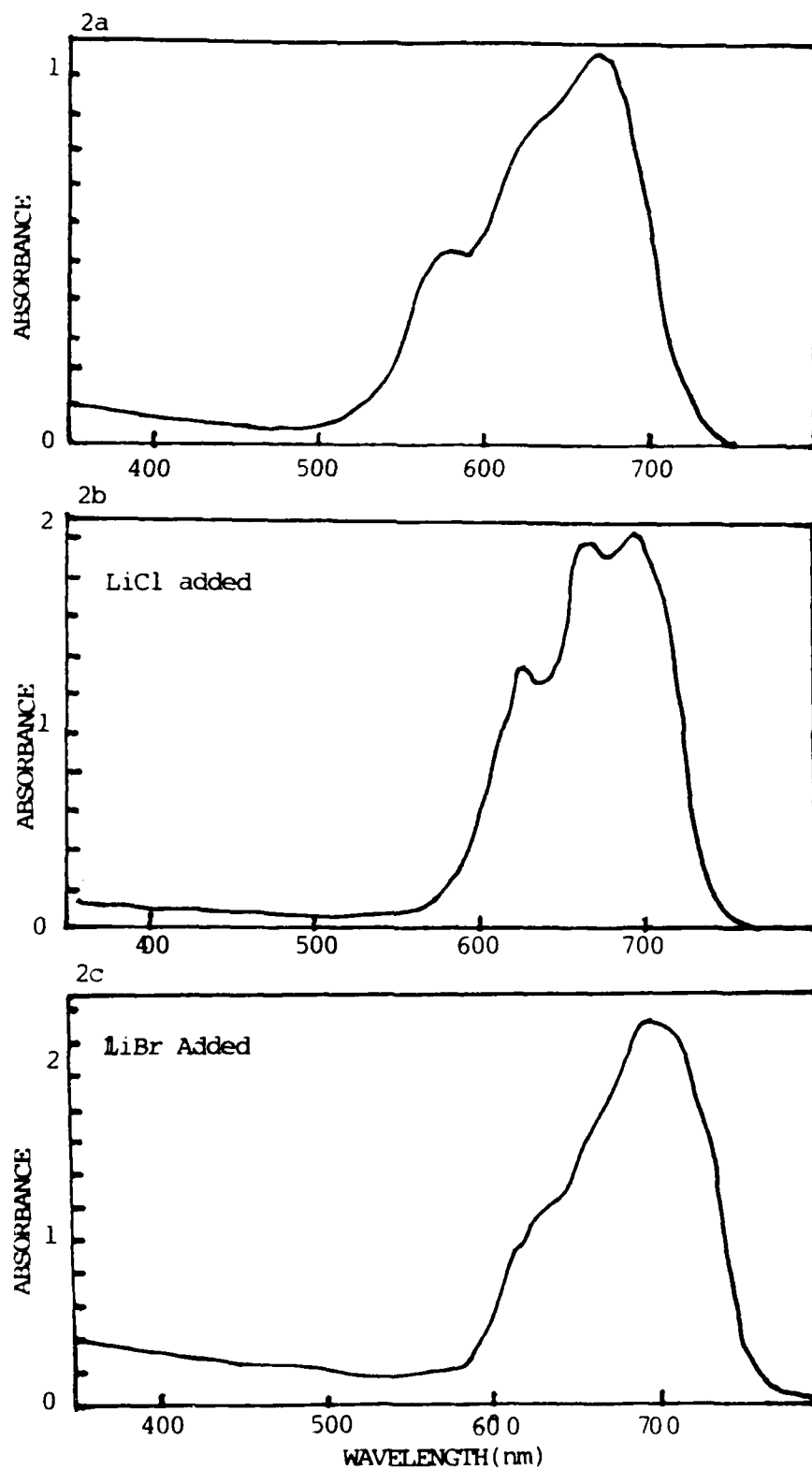
Optical spectrum of cobaltous chloride in
tetrahydrofuran.
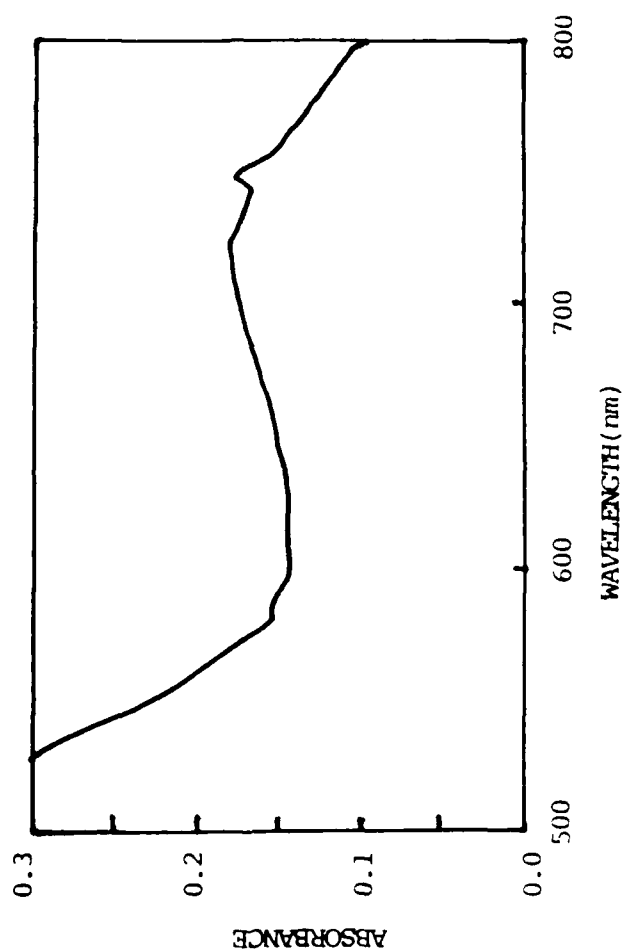
Optical spectrum of nickel containing film.

ELECTROCHEMICAL STUDIES
OF
METAL COMPLEXES

Rationale

Within the polymer electrode the metal complexes are expected to effect the electron transfer catalysis required for the carbon monoxide fuel cell. The reaction to be catalyzed is the two electron oxidation of carbon monoxide to carbon dioxide.

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^-$$
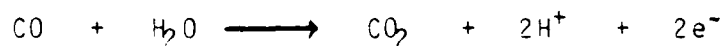
Catalysis of this reaction will depend on both the electrochemical and substitution properties of the metals involved. To explore the potential of various metal complexes as electron transfer catalysts, the electrochemistry of several metal complexes has been undertaken. Under study are $[Co(tet-b)Cl_2]^+$ and $[Fe(tet-b)(CH_3CN)_2]^{2+}$. These are the free ion versions of the complexes which are being prepared in polymer matrices. Polymer attachment is not expected to seriously affect the thermodynamics of the reactions.

Voltammetric Study of the $[Co(tet-b)Cl_2]^+$ Ion

Aqueous solutions of the $Co(tet-b)Cl_2]^+$ ion with 0.10 M potassium chloride as supporting electrolyte were subjected to cyclic voltammetric analysis. A shiny platinum electrode (0.0030 cm^2 geometric area) was used as an indicator electrode and a saturated calomel electrode as a reference electrode. The solutions were deaerated with bubbling nitrogen before scanning, although the scans themselves were made on quiescent solutions. Scans were begun at potentials positive relative to the

Co(III)/Co(II) couple and the scans were from cathodic to anodic and back. The rates were varied from 7 to 50 mV/s.

In all cases both oxidation and reduction waves were observed. In all cases the electrode process was _psuedo_ reversible with the anodic peak current essentially equal to the cathodic peak current (figure 15). Plots of the square root of the scanning rate _versus_ the cathodic peak current were linear which indicates that the rate of the electrode process is limited by the rate of diffusion of reactants to its surface rather than any rate limiting step during electron transfer (figure 16).

TABLE

Scanning Rate (mV/s)	Peak Potentials (mV, vs SCE)		Peak Cathodic Current (μA)	Half Wave Potential (mV, vs SCE)
	Cathodic	Anodic		
7	70	150	10.5	122
14	65	150	15.5	110
21	60	155	20.0	105.5
28	65	155	25.3	105
50	50	165	29.5	102

Cyclic voltammetric data for scans of the $[Co(tet-b)Cl_2]^+$ ion.

The apparent simplicity of the reaction is deceptive, because the half-wave potential is dependent of scan rate. At the more rapid scanning rates the half-wave potential becomes more or less constant. The simplest electrode process would be

$$1e^- + [Co(tet-b)Cl_2]^+ \longrightarrow [Co(tet-b)Cl_2]^0$$
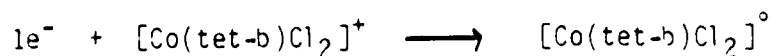
However, cobalt(II) is kinetically labile and undergoes a large Jahn-Teller
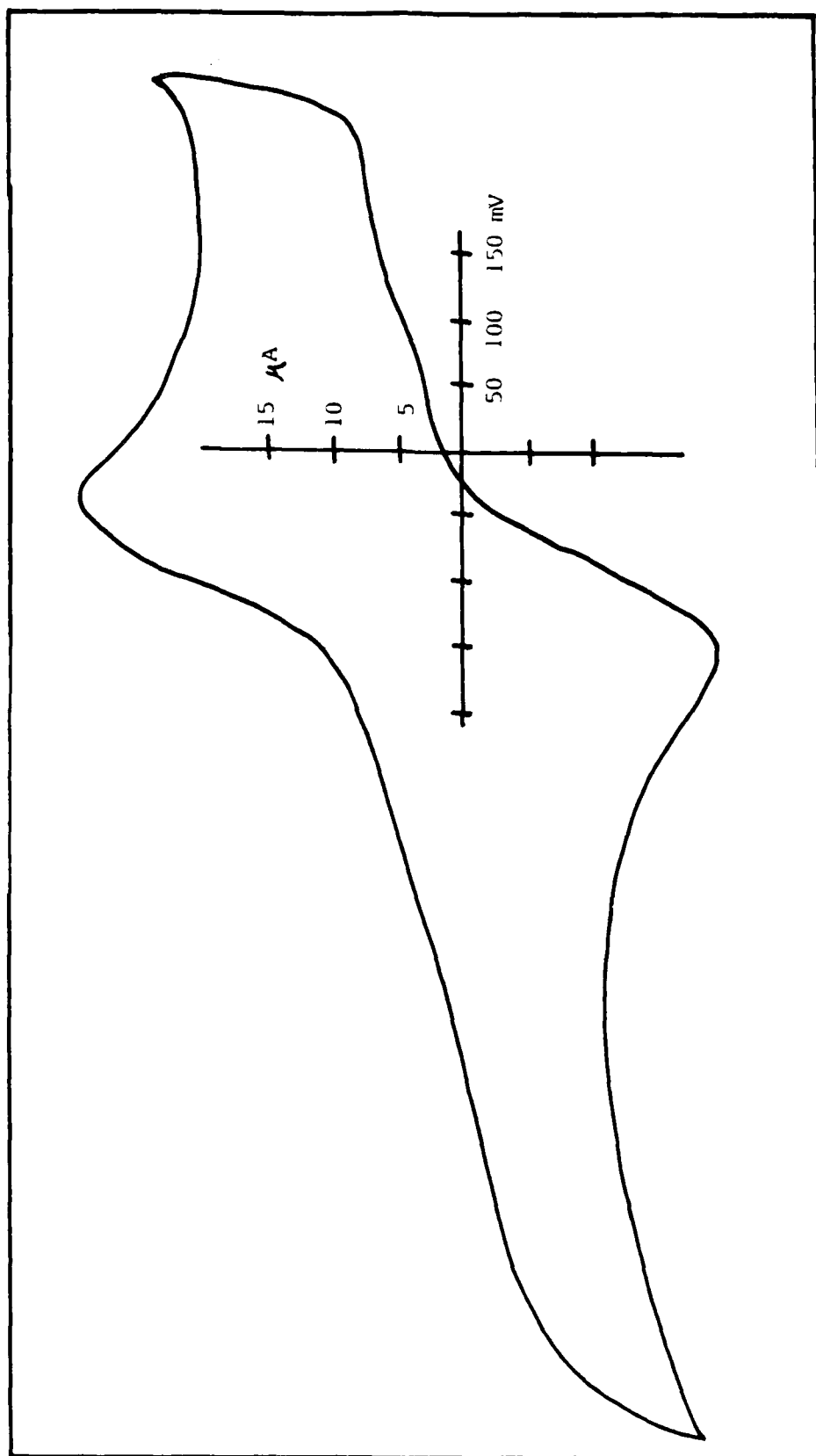
Cyclic voltammetry of $[Co(tet-b)Cl_2]^{+1}$, scanning rate 50.0 mV/s.

$[Co(tet-b)Cl_2]^+$

Square Root of Scanning Rate
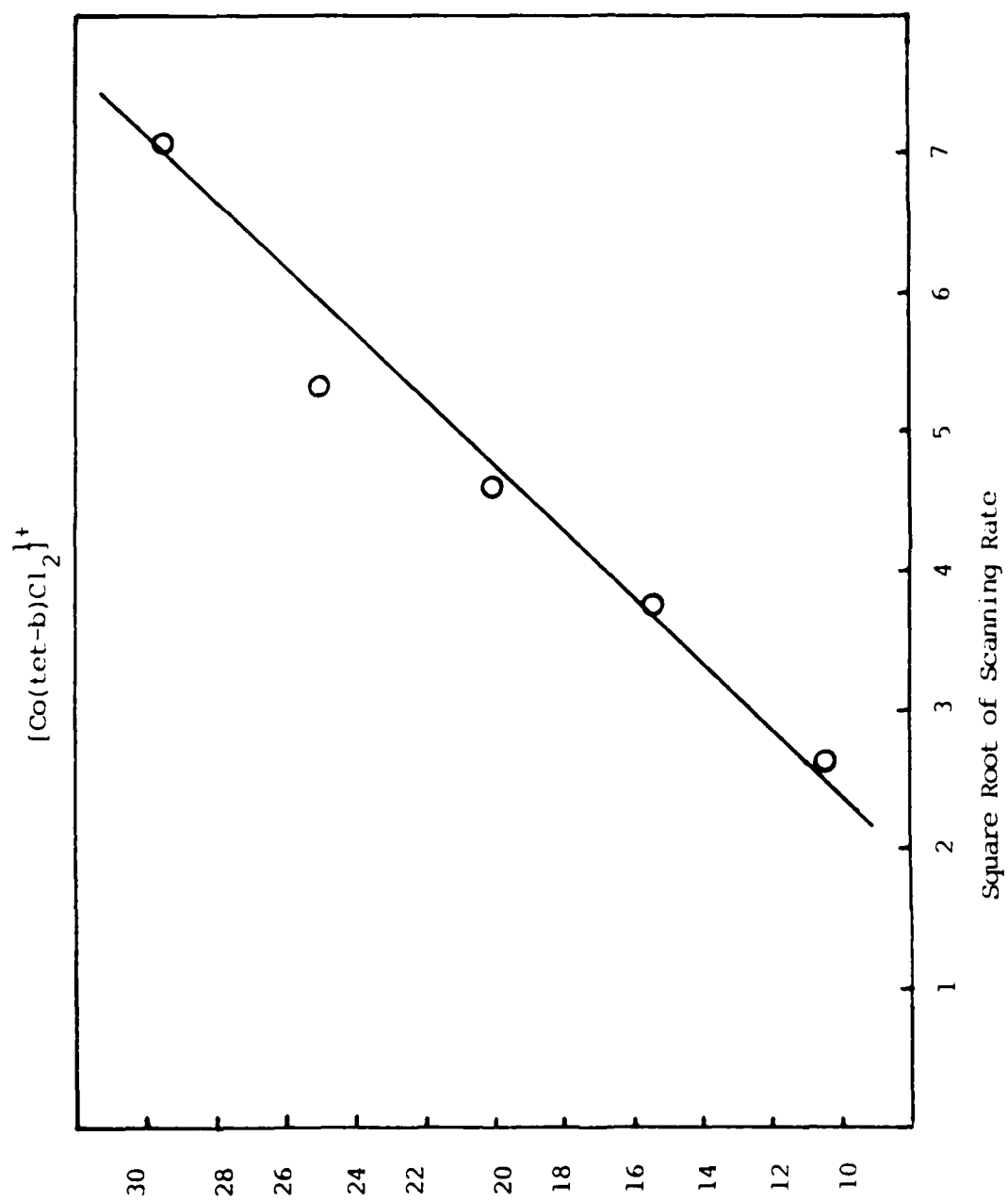
tetragonal distortion, which labilizes the chlorides and leads to facile dissociation

$$[Co(tet-b)Cl_2]^o \longrightarrow [Co(tet-b)]^{2+} + 2Cl^-$$

This latter reaction is supported by bulk electrolysis experiments during which the spectrum of the electrolyte is monitored. In such experiments decomposition of the $[Co(tet-b)Cl_2]^o$ is implicated. This latter process may be slow on the cyclic voltammetry time scale, hence the peak anodic and cathodic currents are equal. Alternatively, the rates may be comparable and what is being observed is the reduction of both $[Co(tet-b)Cl_2]^o$ and $[Co(tet-b)]^{2+}$ at similar potentials. The shift in the half-wave potential at the slower scanning rates would be an indicative response to this latter process. A third alternative is that since the reaction given above is reversible, the presence of the supporting electrolyte, KCl, may have shifted the equilibrium above sufficiently to the left that dissociation is suppressed.

Because of the large ligand field strength of the nitrogen macrocycle the three plus oxidation state is favored over the divalent state. It is therefore expected that molecular oxygen would effect the re-oxidation the cobaltous product. If the oxidation is sufficiently rapid, no anodic wave will be oberved. If, on the other hand, oxidation is at a comparble rate, a diminished anodic wave results.

$$2H^+ + 2[Co(tet-b)Cl_2]^o + O_2 \longrightarrow 2[Co(tet-b)(H_2O)Cl^+]^{2+} + Cl^- + H_2O_2$$
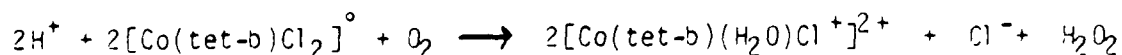
Scans of oxygen saturated solutions exhibited only a cathodic wave which is supportive of rapid oxidation by molecular oxygen (figure 17). Furthermore, the cathodic wave was shifted to more negative potentials by 20-30 mV, and
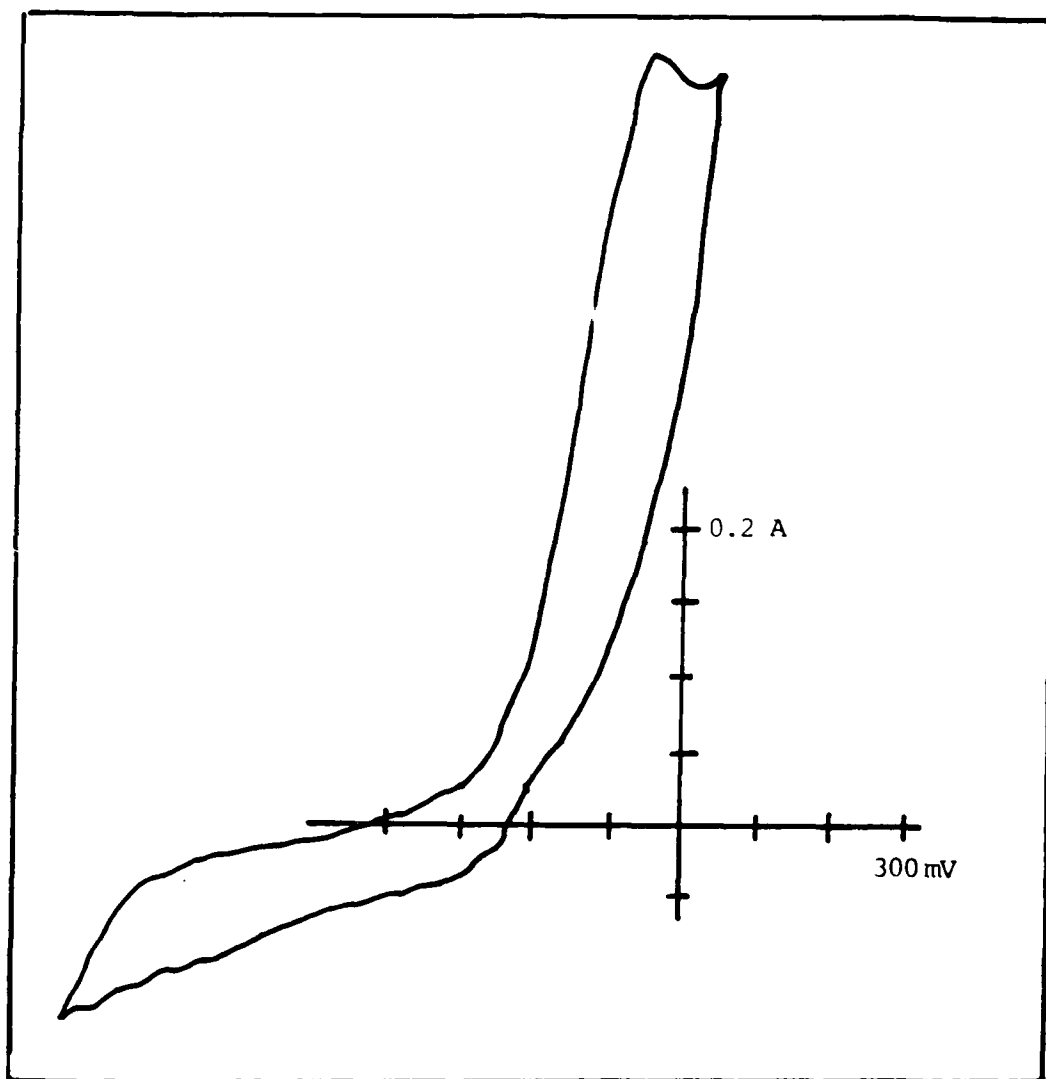
Cyclic Voltammetry of $[Co(tet-b)Cl_2]^{2+}$
Scanning Rate 45 mV/s

had much larger peak currents.

Scanning Rate (mV/s)	Peak Cathodic Current (μA)
80	59
150	74
200	83
250	89
350	94
450	105

Cyclic voltammetric data for $[Co(tet-b)Cl_2]^+$ in oxygen saturated solutions

Plots of the square root of the scanning rate <u>versus</u> the cathodic peak potential were linear which again indicates a diffusion controlled process (figure 18).

In the presence of oxygen it is proposed that the product of the reduction is rapidly re-oxidized by molecular oxygen. The aquo-chloro product is proposed, because a bridging dioxygen dimer is expected as a reaction intermediate

$$[Cl(tet-b)Co-O_2-Co(tet-b)Cl]^{2+}$$
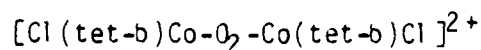
In that re-oxidation by oxygen generates new species for reduction, the cathodic current is the result of reduction of $[Co(tet-b)Cl_2]^+$ and the re-oxidation products. This would explain the shift in potential as well as the increased cathodic currents, Thus the diffusional behavior of the electrode process may result from diffusion of oxygen to the electrode surface rather than $[Co(tet-b)Cl_2]^+$ diffusion. The process actually being observed would then be the catalytic reduction of moleuclar oxygen.

Voltammetric Study of the $[Fe(tet-b)(CH_3CN)_2]^{2+}$ Ion

Aqueous solutions of the $[Fe(tet-b)(CH_3CN)_2]^{2+}$ ion were prepared

$[Co(tet-b)Cl_2]^{1+}$ in oxygen saturated solution

Square Root of Scanning Rate
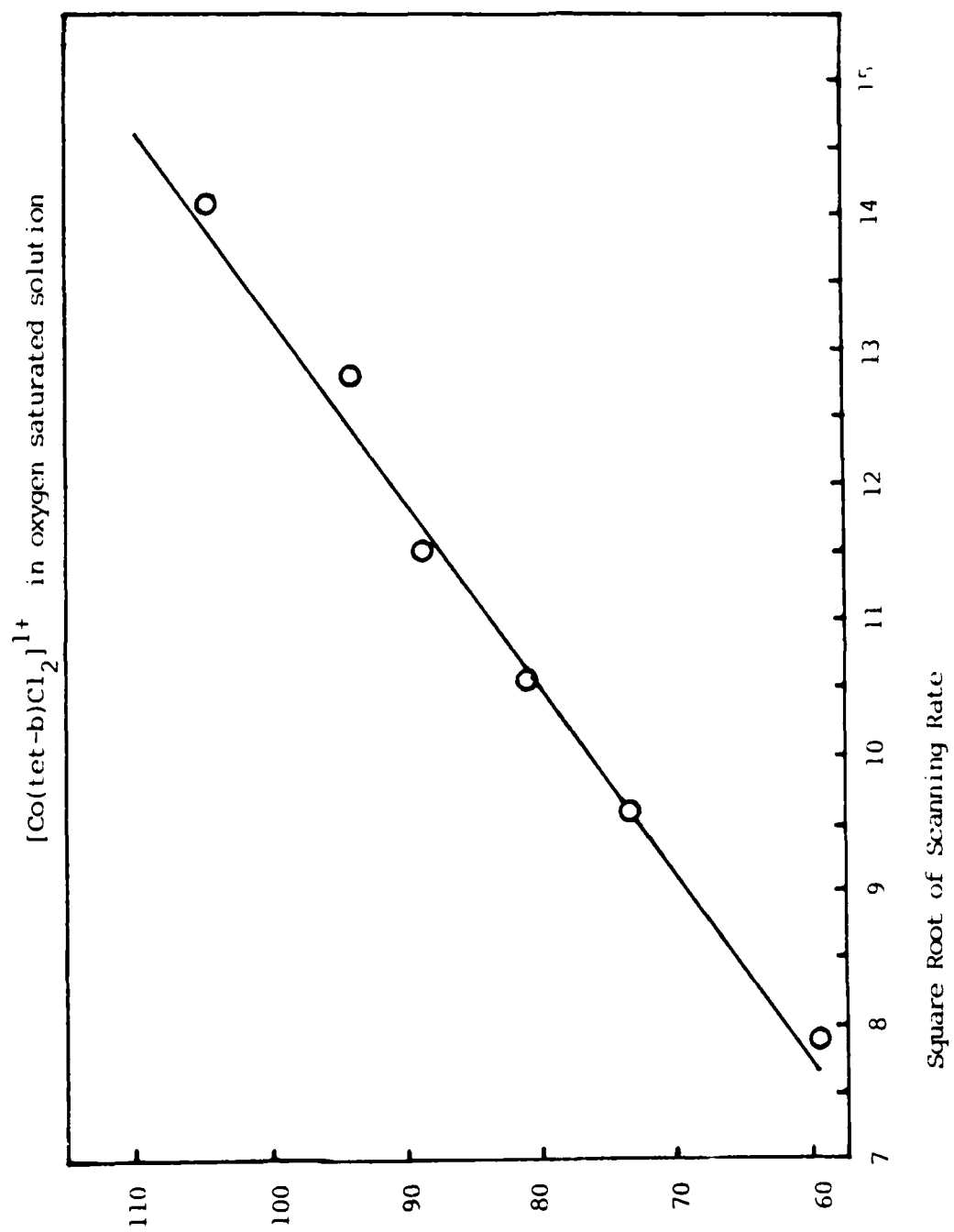
in 0.20 M potassium chloride as a supporting electrolyte, and subjected to cyclic voltammetric anal s. A shiny platinum electrode was used as a working electrode (0.0030 cm² geometric area) and a calomel reference, electrode was used. The solutions were deaerated with bubbling nitrogen, but analyses were carried out on quiescent solutions.

The region -1200 to + 700 versus SCE mV was scanned over which two cathodic and two anodic waves were observed. The more positive wave at 315 mV was assigned to the Fe(III)/Fe(II) couple (figure 19), and the more cathodic wave at -524 mV was assigned tenatively to a Fe(II)/Fe(I) couple (figure 20). The Fe(III)/Fe(II) couple was examined over a scaning rate of 50 to 200 mV/s and its half-wave potential was independent of the scanning rate. For all scanning rates used the reaction was irreversible as indicated by a smaller anodic current than cathodic current. For all scans the anodic current was less than 70% of the cathodic current, thus indicating a large degree of irrevisibility. This irreversibility is not be unexpected, however, since any process would be complicated by the dissociation of the weakly held acetonitrile ligands. Spectral anaylsis of aqueous solutions of $[Fe(tet-b)(CH_3CN)_2]^{2+}$ revealed that the acetonitriles are essentially dissociated.

TABLE

Scanning Rate (mV/s)	Peak Cathodic Current (μA)	Peak Anodic Current (μA)	Half Wave Potential (mV)
25	104.7	31.8	-480.0
100	194.1	50.4	-503.5
200	314.3	124.8	-501.1
400	400.0	105.9	-524.5
800	424.7	75.6	-547.9

Cyclic voltammetric data for scans of the $[Fe(tet-b)(CH_3CN)_2]^{2+}$ ion.
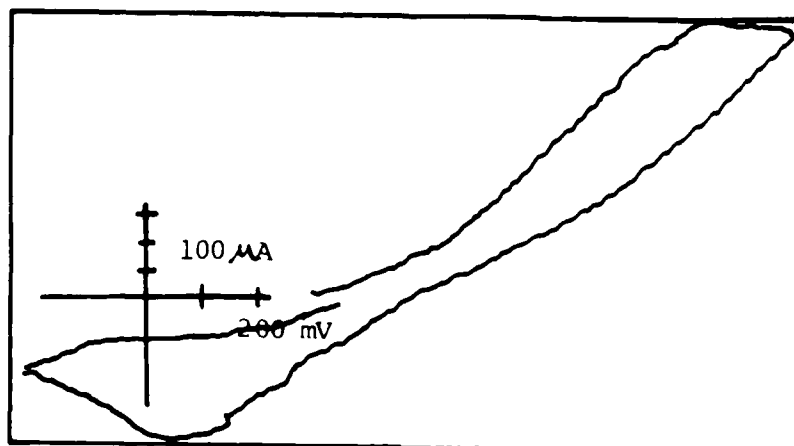
Cyclic voltammetry of $[Fe(tet-b)(CH_3CN)_2]^{2+}$
Scanning rate 16000 mV/s.
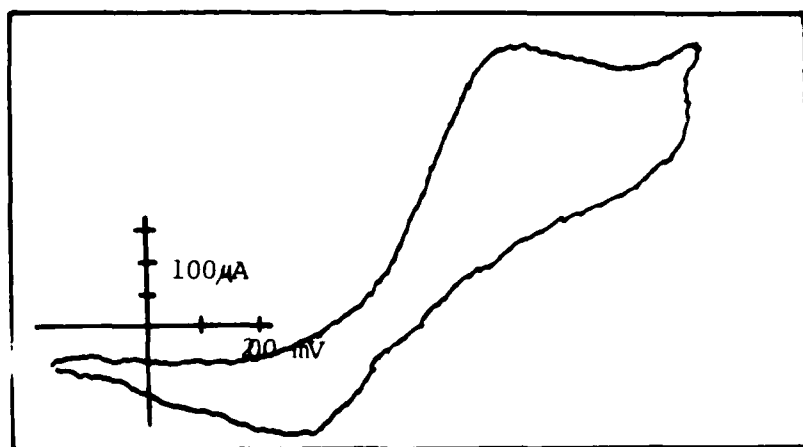
Cyclic voltammetry of $[Fe(tet-b)(CH_3CN)_2]^{2+}$
Scanning rate 25 mV/s.

$[Fe(tet\text{-}b)(CH_3CN)_2]^{2+}$

Cyclic voltammetry of $[Fe(tet\text{-}b)(CH_3CN)_2]^{2+}$
Scanning rate 200 mV/s.

$$[Fe(tet-b)(CH_3CN)_2]^{2+}$$

Square Root of Scanning Rate
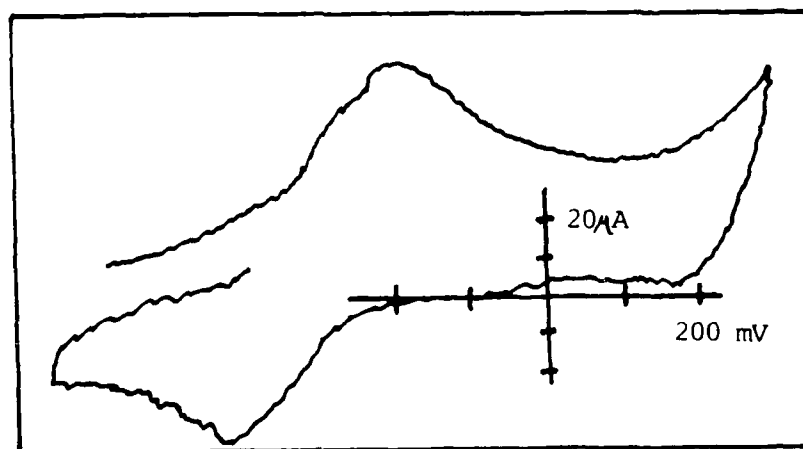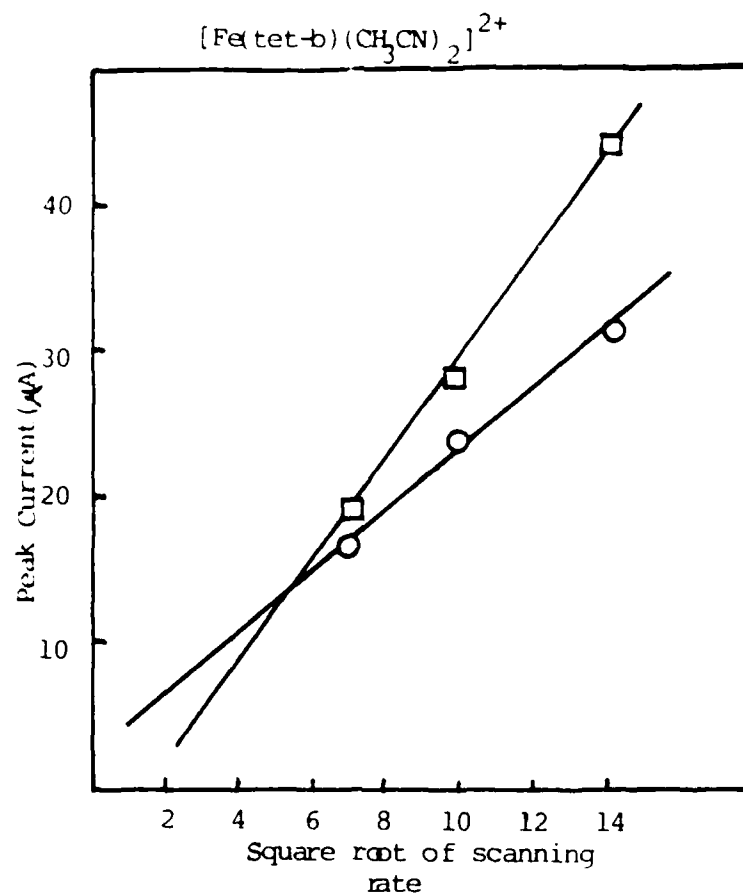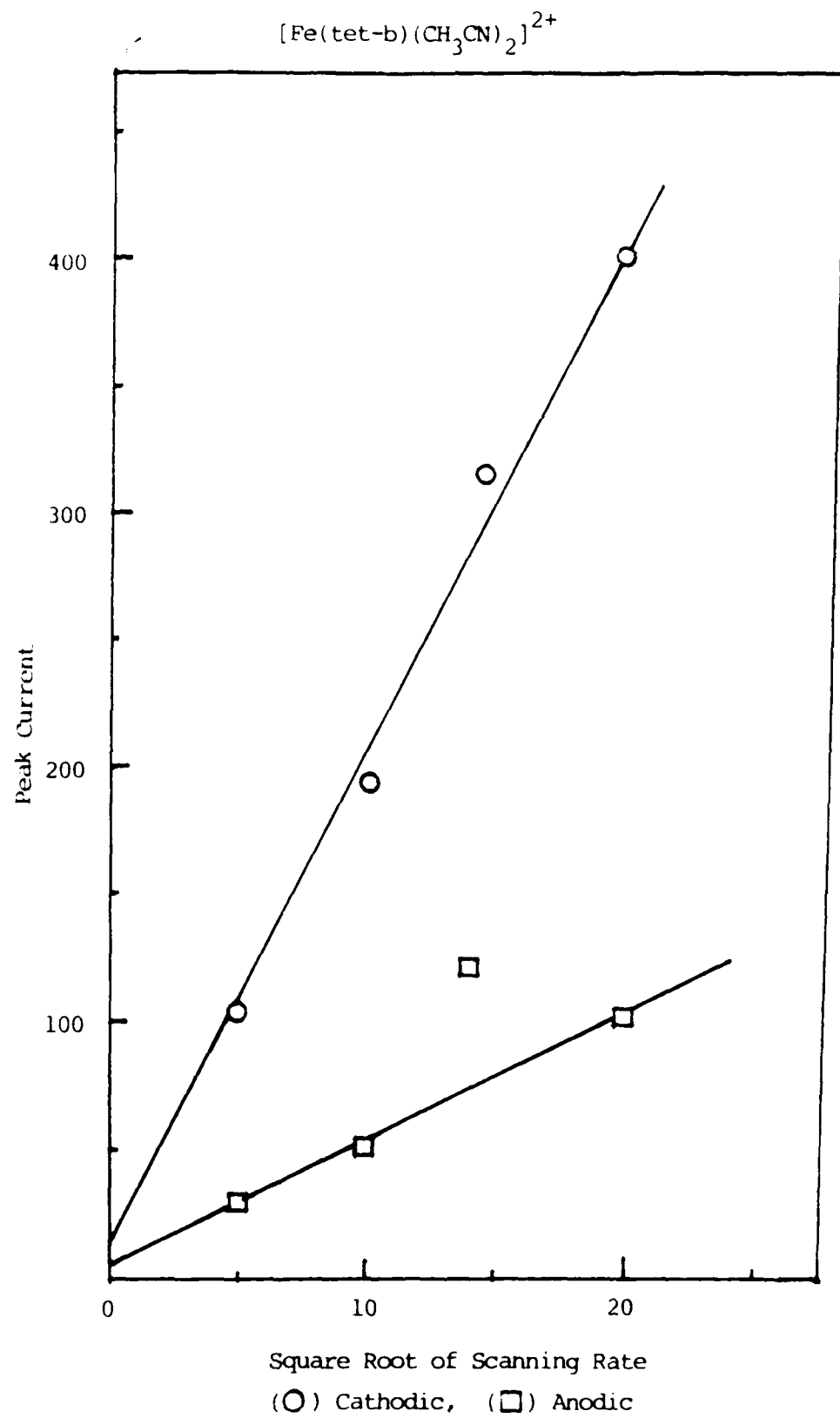
(O) Cathodic,   (□) Anodic

The half-wave potential of the Fe(II)/Fe(I) couple ranged from -450 to -592 mV's for a scanning rate range of 25 to 1600 mV's. There were much larger cathodic currents compared to anodic currents which again is indicative of an irreversible electrode process. Plots of the square root of the scanning rate versus the peak currents were linear indicating that the rate controlling process was diffusion to the electrode surface. In this case the half-wave potential was dependent on the scan rate and tended to become more negative as the scan rate increased.

RELEVANT EXPERIMENTAL
TECHNIQUES

In this section no attempt is made to describe all of the methods and techniques employed in this study. Rather, mention is made of those methods and techniques which are non-standard or the explaination of which is necessary for optimal interpretation of the results.

Optical Spectra of Thin Films

In many cases it was of interest to determine the optical spectra of thin polymer films (ca. 100 microns). Because of the problems arising from light scattering during the recording of the spectra, a repetitive scanning technique was used to average out the scattering fluctuations and thus reduce the signal-to-noise ratio. Films were mounted on a quartz disk, and the spectrum was recorded four to eight times using a Hitachi model 100-60 spectrophotometer interfacedd to an Apple II plus microcomputer. After each scan the spectrum was stored and the sample was rotated 10-20°. The accumulated spectra were average with a considerable reduction in signal-to-noise ratio in the result (figure 21). Spectral averaging was done by a point-by-point addition of the spectra. Further filtering was carried out using a quadratic least squares fit to small segments of the spectrum. The software used for data collection and manipulation was developed in these laboratories.

Cyclic Voltammetry

The cyclic voltammetry studies were carried out using the three electrode arrangement. The working potential was supplied by a Bioanaytical
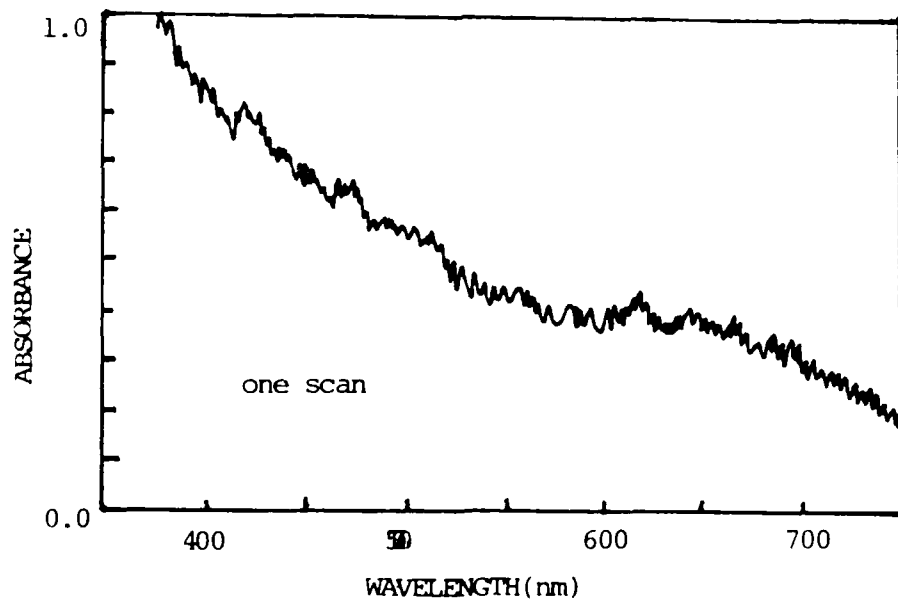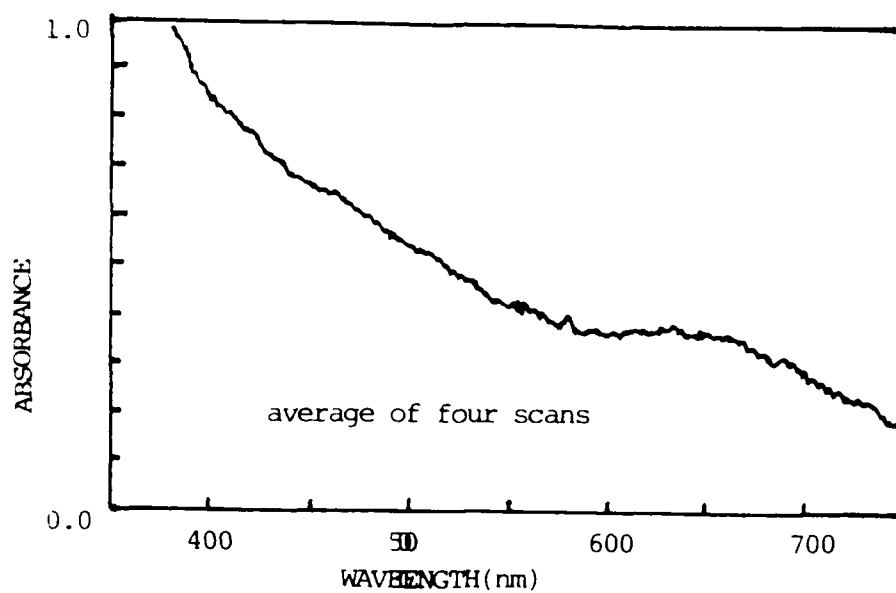
The effect of repetitve scanning on the optical spectrum of films.

model CV-1V potentiostat, and IBM cells and electrodes were used. The work-
ing and indicator electrodes were platinum, and a saturated calomel elect-
rode was used as a reference electrode for aqueous solutions and a silver-
silver chloride reference electrode equipped with salt bridge was used for
non aqueous solutions. The voltammograms were recorded using an x-y record-
er or an Apple II plus microcomputer and software developed in these labora-
tories.

Aqueous $[Fe(tet-b)(CH_3CN)_2]^{2+}$ and $[Co(tet-b)Cl_2]^{1+}$ Solutions

The $[Fe(tet-b)(CH_3CN)_2]^{2+}$ and $[Co(tet-b)Cl_2]^+$ ions were prepared as
the perchlorate salts. The solubilities of these salts was insufficient to
yeild good cyclic voltammetry results. To prepare aqueous solutions in
0.10 M or 0.20 M potassium chloride as a supporting electrolyte, ca. 40
mg samples of the perchlorate salts were absorbed on 1 cm x 1 cm^2 column
of Sephadex C-25 cation exchange resin in the potassium form. This was
washed with several volumes of water, then eluted with 2.5 mL of 1 M KCl.
The eluent was then diluted to 25 mL.

Determination of Ionic Chloride and Iodide

Aqueous solutions containing chloride or iodide were titrated with a
standard silver nitrate solution. The progress of the titration was moni-
tored using a silver indicator electrode and calomel reference electrode.
In cases in which both chloride and iodide were present endpoints for both
halides could be detected (figure 22).

Determination of Covalent Chloride (Polymers)

Polymers containing benzylic chloride were refluxed in pyridine. The
resulting mixture was acidified with acetic acid and standard silver ni-
trate added. The excess silver nitrate was determined by titration against

VOLUME OF TITRANT (mL)
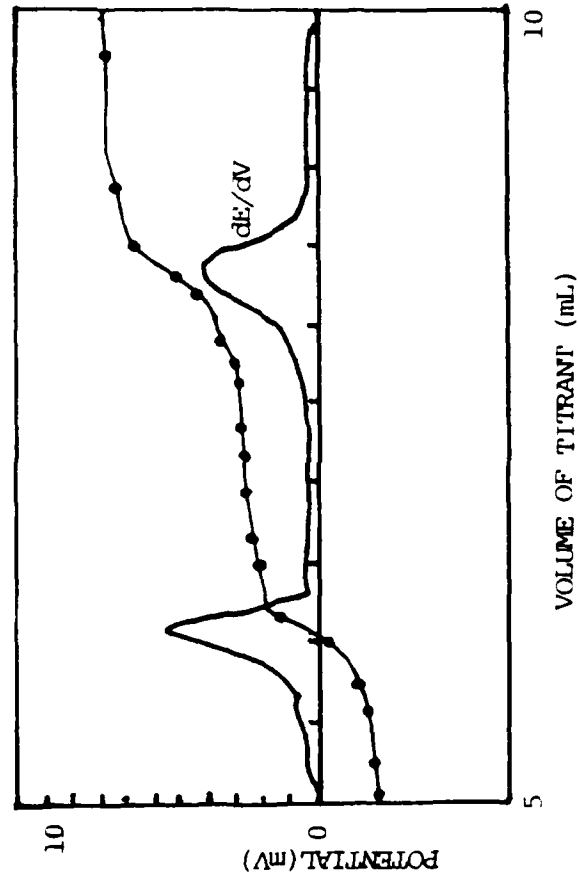
Typical potentiometric titration of an aqueous solution containing both chloride and iodide.

standard ammonium thiocyanate.

Determination of Cobalt in Polymer Samples

Cobalt containing polymer samples were digested in sulfuric acid-hydrogen peroxide by treating ca. 30 mg of sample with 1 mL of concentrated

sulfuric acid and 1 mL of 35% hydrogen peroxide. This was heated strongly on a hot plate until fuming began. More hydrogen peroxide was added and heating resumed until funning commenced once more. The process was repeated until all material had dissolved.

The resultant pink solution was diluted with water and 1 mL of 1.0 M hydroxylamine hydrochloride was added. After boiling for 5 min. 1.5 mL of 7.5 M ammonuim thiocyanate was added. The resulting solution was extracted with methyltertiarybutylketone and the optical density measured at 620 nm.

Determination of the Extent of Gelation

The extent of gel formation during the reaction of chloromethylated polystyrene and the tetraamine, tet-a, was determined. The reaction was carried out by refluxing the reagents in tetrahydrofuran. During the course of the reaction samples were removed from the reaction mixture. To each sample 5 mL of ethanol was added to precipitate the polymer. This separated the polymer from the tetraamine. The polymer was dried and weighed. The polymer was treated with 30ml of toluene and the undissolved solid filtered and weighed. This latter solid is the gel which is in soluable, whereas the non-gelled material is toluene soluble. From the weight of the polymer sample and the gel weight the extent of gelation is determined.

SUMMARY

It has been proposed that polymer bound metal complexes be investi-
gated as potential electrode-catalysts for a carbon monoxide fuel cell.
The problems addressed in this investigation are synthesis and character-
ization of polymer bound metal complexes and the chemical and electrochem-
ical behavior of selected metal complexes in solution and in polymer
matrices. The supporting polymer matrices of interest were polystyrene,
polyvinyl alcohol and polyvinyl chloride. Of these polystyrene was found
to hold the greatest promise. The methods for activating these polymers
were examined, and ligand containing polymers were prepared. These were
prepared as swollen gels and as thin films. We have not yet been able to
prepare pendant ligand polymers in solution. The metals cobalt, nickel and
iron were studied. Cobalt and nickel were incorporated into polymers and
the resulting materials were studied.

CURRICULUM VITAE

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BIRTHDAY:	May 6, 1947
MARITAL STATUS:	Married, two children

EDUCATION:

1952 - 1965   Chicago Public and Archdiocesan
School Systems
Chicago, Illinois

1965 - 1969   University of Illinois
at Chicago Circle
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B. S., December, 1969
Major - Chemistry

1970 - 1973   Northwestern University
Evanston, Illinois
M. S., June, 1971
Major - Inorganic Chemistry
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EMPLOYMENT:

1970 - 1973   Teaching Assistant
Northwestern University
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1973 - present   Associate Professor
Atlanta University
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1980 - 1981   Visiting Professor
University of Southern California
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AFFILIATIONS:

American Chemical Society
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RESEARCH INTERESTS   Metal Complex Photochemistry - photochemistry and
                            photophysics of metal complexes with a special
                            interest in oxidation-reduction processes and in
                            the photochemistry of the azido group.

                            Polymer Bound Metals - synthesis and characteriza-
                            tion of transition metal complexes covalently
                            bound to organic polymer matrices.

                            Chemical Reactivity - studies of the effectiveness of
                            chemical potential and electronegativity in predicting
                            the reactivity of small molecules.

ADDITIONAL RESEARCH   1980-81 - visiting scientist at the University of
                            Southern California; collaborated with Dr. Arthur
                            W. Adamson on problems related to the photochemistry
                            and photophysics of chromium(III) complexes.

                            Summer 1986 - NASA Summer Faculty Fellow (Power
                            Systems Division); investigated advanced energy
                            storage systems to be used on the space station
                            which is under development.

TEACHING EXPERIENCE: Atlanta University

                                Physical Chemistry - chemical kinetics

                                Advanced Inorganic - structure, spectroscopy and
                                Chemistry   reactivity of inorganic
                                                      molecules

                                Physical Inorganic - advanced topics in inorganic
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                                Instrumental Analysis - theory and application of
                                                      instrumental methods

                                Introduction to Pascal - basics of programming

                                Thesis Supervision - supervised ten M.S. degree
                                                     students in various areas of
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                            University of Southern Californi

                                Freshman Chemistry

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PROFESSIONAL SERVICE: refereed numerous scientific articles and research proposals.

annually served as a judge in the Atlanta Science Congress.

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supervised several high school students' research projects.

performed the pre-publication review of Braun's "Instrumental Analysis".

active member of the Continuing Education Committee of the American Chemical Society, local section. This Committee has developed and sponsored a number of seminars, symposia and workshops.

UNIVERSITY SERVICE: served for three years in the development of the University's first Faculty Handbook. I served one term as chair of that Committee.

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served on the departmental library, recruitment, admissions, faculty recruitment, and space utilization committees.

GRANTS AWARDED: Petroleum Research Fund on metal nitrenes

National Institutes of Health on model photosynthetic systems

National Aeronautics and Space Administration on metal azide photochemistry

National Aeronautics and Space Administration on iron oxidation-reduction photochemistry

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PUBLICATIONS: J. L. Reed, F. Wang and F. Basolo, "Coordinated Nitrene
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Z. Lu, E. Nyairo and J. L. Reed, "Metal Complexes in Polymer Matrices", manuscript in preparation.

END
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